

## SUPPORTING INFORMATION

# A Dioxane Template for Highly Selective Epoxy Alcohol Cyclizations

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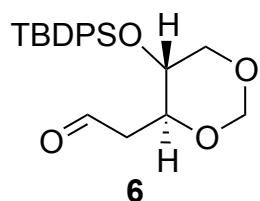
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**General Considerations:** All reactions were run under aerobic conditions (air) with flame-dried glassware using standard techniques for manipulating air-sensitive compounds unless otherwise stated. Anhydrous solvents were obtained by filtration through drying columns or by distillation over sodium and calcium hydride.

Flash column chromatography was performed using 230-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm), aqueous potassium permanganate, vanillin, and/or *p*-anisaldehyde. Preparative High Performance Liquid Chromatography was performed using normal phase elution on a system equipped with simultaneous diode array UV detection. Data are reported as follows: (column type, eluent, flow rate: retention time ( $t_r$ )). Automated flash chromatography was performed using Biotage Isolera One Instruments.

Nuclear magnetic resonance spectra were recorded either on 300, 400, 500, or 600 MHz Bruker or Varian spectrometers. Chemical shifts for  $^1\text{H}$  NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform,  $\delta = 7.27$  ppm or benzene,  $\delta = 7.15$  m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for  $^{13}\text{C}$  NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.36 ppm), or  $\text{C}_6\text{D}_6$  (128 ppm) as the internal standard. Optical rotations were measured on a Jasco Model 1010 polarimeter at 589 nm. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer by Eric Standley. Infrared spectra were recorded using an Agilent Cary 630 FTIR. Gas chromatography (GC) data was collected on a Varian CP-3800 GC using an Agilent CHIRALDEX Y-TA column (30m x 0.25 mm).

**Reagents:** Commercial reagents were used as supplied or purified by standard techniques where necessary.



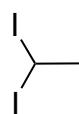
**2-((4S,5R)-5-((tert-butyldiphenylsilyl)oxy)-1,3-dioxan-4-yl)acetaldehyde**

**Note:** On large scale (>5 g), ozonolysis was difficult. The reaction times required for full conversion of enoate **S2** stretched to many hours, making the procedure impractical. Furthermore, yields from ozonolysis were lower on such scale. We thus recommend the use of a two-step dihydroxylation/ oxidative cleavage protocol on large scale.

***Preparation via dihydroxylation and oxidative diol cleavage:***

To a solution of enoate **S2** (0.730 g, 1.6 mmol) in 1:1 v/v  $\text{H}_2\text{O}$ :*t*-BuOH (1.6 mL) was added citric acid (252 mg, 1.2 mmol), a solution of NMO in  $\text{H}_2\text{O}$  (50% by weight, 412 mg of solution, 365 mL, 206 mg NMO, 1.76 mmol), and  $\text{K}_2\text{OsO}_2(\text{OH})_4$  (2.9 mg, 0.008 mmol). The resulting green colored slurry was stirred vigorously for 21 h at ambient temperature. Over this time the reaction solution became colorless but remained opaque. The reaction was quenched with 1 M  $\text{HCl}_{(\text{aq})}$  (~2 mL), and the crude solution was extracted with  $\text{Et}_2\text{O}$  (3 x ~10 mL), and the combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo* to give the crude diol ( $R_f = 0.10$  (1:4 EtOAc, hexanes)), which was carried into oxidative cleavage without further purification.

The crude diol from the preceding step was dissolved in 1:1 v/v THF: $\text{H}_2\text{O}$  (8.0 mL). The solution was cooled to 0 °C, and  $\text{NaIO}_4$  (1.03 g, 4.8 mmol) was added. The reaction mixture was stirred vigorously for 1.5 h at 0 °C. It was then quenched by dilution with  $\text{H}_2\text{O}$  (~15 mL). The mixture was extracted with EtOAc (3 x ~30 mL), and the combined organics were washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (gradient 5% to 40% EtOAc in hexanes) to provide **4** (505 mg, 82% over 2 steps).  $R_f = 0.44$  (1:4 EtOAc, hexanes).  $[\alpha]_D^{22} = -6.5$  ( $c = 1.26$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.71 (dd,  $J = 2.6, 1.4$  Hz, 1H), 7.68–7.61 (m, 4H), 7.51–7.38 (m, 6H), 4.87 (d,  $J = 6.2$  Hz, 1H), 4.58 (d,  $J = 6.2$  Hz, 1H), 4.00 (app td,  $J = 9.0, 2.8$  Hz, 1H), 3.90 (dd,  $J = 10.7, 4.9$  Hz, 1H), 3.57 (app td,  $J = 9.4, 5.0$  Hz, 1H), 3.40 (app t,  $J = 10.3$  Hz, 1H), 2.80 (ddd,  $J = 16.6, 2.8, 1.4$  Hz, 1H), 2.41 (ddd,  $J = 16.6, 9.1, 2.7$  Hz, 1H), 1.06 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.7, 135.9, 135.9, 133.3, 132.7, 130.5, 130.4, 128.2, 128.0, 93.3, 77.5, 71.6, 67.1, 45.8, 27.1, 19.4. FTIR (thin film, NaCl) 3072, 2932, 2858, 1729, 1473, 1428, 1217, 1171, 1111, 1066, 1035  $\text{cm}^{-1}$ . HRMS (ESI) Calcd for  $\text{C}_{22}\text{H}_{28}\text{O}_4\text{Si} [\text{M}+\text{Na}]^+$ : 407.1649, found 406.1660.



**1,1-Diiodoethane (**S1**).**

Prepared according to literature procedure.<sup>1</sup> 1,1-Dichloroethane (15 mL, 177 mmol) and iodoethane (43 mL, 531 mmol) were added to a dry round-bottomed flask equipped with a stir bar and reflux condenser. To this was added  $\text{AlCl}_3$  (2.3 g, 17 mmol), and the resulting mixture was refluxed at 100 °C for 4 h, after which was cooled to 0 °C on an ice bath. Added ~100 mL  $\text{Et}_2\text{O}$ , washed with 10% aqueous thiosulfate, dried with  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Purification by column chromatography (100% pentane) afforded **S1** as a yellow oil that rapidly turns red when exposed to light (20.0 g, 40%).  $R_f = 0.67$  (100% pentane).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.23 (q,  $J = 6.7$  Hz, 1H), 2.93 (d,  $J = 6.7$  Hz, 3H). Spectrum matches a commercial standard.

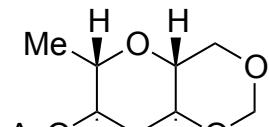
<sup>1</sup> Letsinger, R. L.; Kammeyer, C. W. *J. Am. Chem. Soc.* **1951**, 73, 3376.

### Acetylation Data

Acetylation of the free hydroxyl group of the cyclized product was used to help confirm the formation of the 6,6 *endo* or the 6,5 *exo* products. Upon the addition of the acetyl group, the proton of the carbinol bearing the OAc would exhibit an upfield shift in the <sup>1</sup>H NMR spectrum, while the rest of the chemical shift would remain largely unchanged. With this identification gCOSY analysis could be used to verify the connectivity of the cyclic ethers, confirming the identity of the product. The stereochemistry remains known as it is determined by both the 2-deoxyribose and the well-precedented Shi epoxidation.

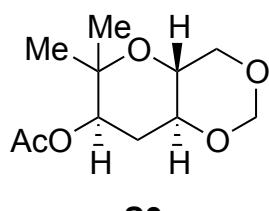
#### General Acetylation Procedure

To a round-bottomed flask charged with the hydroxyl containing cyclic ether (1 equiv) was added CH<sub>2</sub>Cl<sub>2</sub> (0.03M), acetic anhydride (3.5 equiv), Et<sub>3</sub>N (9 equiv), and DMAP (25 mol %). The solution was stirred at rt for 2 h after which sat NH<sub>4</sub>Cl<sub>aq</sub> was added to quench the reaction. Extraction with Et<sub>2</sub>O, drying with MgSO<sub>4</sub>, and concentration under reduced pressure afforded the crude acetylated product that was purified by column chromatography (gradient of 0% to 100% EtOAc in hexanes).



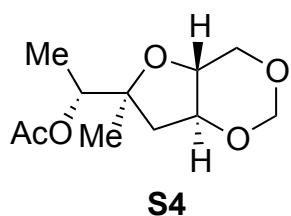
**(4aR,6S,7R,8aS)-6-methylhexahydropyrano[3,2-d][1,3]dioxin-7-yl acetate (S2).**

Prepared according to the general acetylation procedure from alcohol **8** (0.0247 g, 0.142 mmol). Purification by column chromatography (gradient of 0% to 100% EtOAc in hexanes) afforded **S2** as an amorphous white solid (0.028 g, 91%). R<sub>f</sub> = 0.41 (3:7 EtOAc, hexanes). [α]<sub>D</sub><sup>22</sup> = -39.3 (c = 0.19 CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.01 (d, J = 6.2 Hz, 1H), 4.62 (d, J = 6.2 Hz, 1H), 4.58 (ddd, J = 11.1, 9.6, 4.8 Hz, 1H), 4.17 (dd, J = 10.4, 4.6 Hz, 1H), 3.50 (dd, J = 9.5, 6.1 Hz, 1H), 3.42 (t, J = 10.1 Hz, 1H), 3.34-3.26 (m, 2H), 2.48 (dt, J = 11.3, 4.4 Hz, 1H), 2.08 (s, 3H), 1.62 (q, J = 11.3 Hz, 1H), 1.19 (d, J = 6.2 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 170.2, 93.9, 76.4, 76.1, 73.6, 72.2, 69.2, 34.9, 21.3, 17.9. FTIR (thin film) 2924, 2856, 1734, 1453, 1365, 1235, 1161, 1126, 1103, 1075, 1020, 932 cm<sup>-1</sup>. HRMS (ESI) Calcd for C<sub>10</sub>H<sub>16</sub>O<sub>5</sub> (M+Na)<sup>+</sup>: 239.0890, found 239.0884.



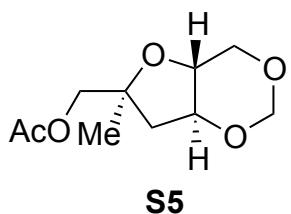
**(4aR,7R,8aS)-6,6-dimethylhexahydropyrano[3,2-d][1,3]dioxin-7-yl acetate (S3).**

Prepared according to the general acetylation procedure from alcohol **19a** (0.017 g, 0.090 mmol). Purification by column chromatography (gradient of 0% to 100% EtOAc in hexanes) afforded **S3** as an amorphous white solid (0.017 g, 86%). R<sub>f</sub> = 0.50 (3:7 EtOAc, hexanes). [α]<sub>D</sub><sup>22</sup> = -7.0 (c = 0.80, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.01 (d, J = 6.1 Hz, 1H), 4.73 (app dd, J = 11.8, 4.6 Hz, 1H), 4.62 (d, J = 6.2, 1H), 4.10 (dd, J = 10.2, 4.5 Hz, 1H), 3.51-3.47 (m, 1H), 3.39 (t, J = 10.1, 1H), 3.30 (m, 1H), 2.27 (app dt, J = 11.3, 4.6 Hz, 1H), 2.07 (s, 3H), 1.72 (q, J = 11.7 Hz, 1H), 1.29 (s, 3H), 1.18 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 170.2, 94.0, 75.0, 73.8, 70.0, 66.9, 31.0, 27.7, 21.4, 18.0. FTIR (thin film) 2989, 2983, 2866, 1731, 1370, 1238, 1166, 1020, 924 cm<sup>-1</sup>. HRMS (ESI) Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>5</sub> (M+H)<sup>+</sup>: 253.1046, found 253.1061.



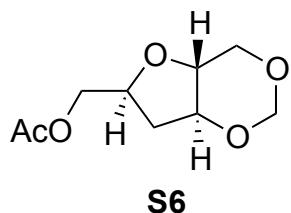
**(*R*)-1-((4a*R*,6*S*,7*a**S*)-6-methyltetrahydro-4*H*-furo[3,2-*d*][1,3]dioxin-6-yl)ethyl acetate (**S4**).**

Prepared according to the general acetylation procedure from alcohol **20b** (0.017 g, 0.084 mmol). Purification by column chromatography (gradient of 0% to 100% EtOAc in hexanes) afforded **S4** as an amorphous white solid (0.012 g, 67%).  $R_f = 0.41$  (3:7 EtOAc, hexanes).  $[\alpha]_D^{22} = -3.8$  ( $c = 0.40$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.09 (d,  $J = 6.2$  Hz, 1H), 4.85 (q,  $J = 6.4$  Hz, 1H), 4.62 (d,  $J = 6.3$  Hz, 1H), 4.40 (app dd,  $J = 9.7$ , 4.2 Hz, 1H), 3.63 (t,  $J = 9.8$  Hz, 1H), 3.48-3.44 (m, 1H), 3.40-3.36 (m, 1H), 2.28-2.24 (m, 1H), 2.09 (s, 3H), 1.74 (t,  $J = 11.4$  Hz, 1H), 1.35 (s, 3H), 1.22 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 94.2, 83.1, 80.4, 74.7, 72.2, 71.7, 38.5, 24.5, 21.5, 15.0. FTIR (thin film) 2983, 2928, 2874, 1736, 1454, 1373, 1242, 1130, 1058, 996  $\text{cm}^{-1}$ . HRMS (ESI) Calcd for  $\text{C}_{11}\text{H}_{18}\text{O}_5$  ( $\text{M}+\text{Na}$ ) $^+$ : 253.1046, found 253.1059.



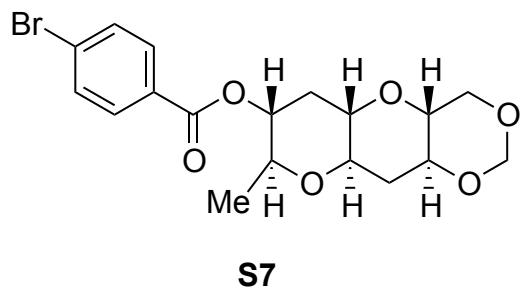
**((4a*R*,6*S*,7*a**S*)-6-methyltetrahydro-4*H*-furo[3,2-*d*][1,3]dioxin-6-yl)methyl acetate (**S5**).**

Prepared according to the general acetylation procedure from alcohol **28** (0.0062 g, 0.036 mmol). Purification by column chromatography (gradient of 0% to 100% EtOAc in hexanes) afforded **S5** as an amorphous white solid (0.0065 g, 91%).  $R_f = 0.39$  (3:7 EtOAc, hexanes).  $[\alpha]_D^{22} = -41.6$  ( $c = 0.27$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.09 (d,  $J = 6.2$  Hz, 1H), 4.62 (d,  $J = 6.3$  Hz, 1H), 4.40 (dd,  $J = 9.6$ , 4.2 Hz, 1H), 3.99 (app q,  $J = 15.2$  Hz, 2H), 3.61 (t,  $J = 9.8$  Hz, 1H), 3.51-3.38 (m, 2H), 2.29 (dd,  $J = 11.8$ , 7.3 Hz, 1H), 2.12 (s, 3H), 1.82 (app dd,  $J = 11.5$ , 11.0 Hz, 1H), 1.39 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 94.3, 80.7, 80.3, 72.7, 71.8, 69.9, 38.5, 24.9, 21.2. FTIR (thin film) 2983, 2928, 2874, 1736, 1454, 1373, 1242, 1130, 1058, 996  $\text{cm}^{-1}$ . HRMS (ESI) Calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_5$  ( $\text{M}+\text{H}$ ) $^+$ : 239.0890, found 239.0903.



**((4a*R*,6*S*,7*a**S*)-tetrahydro-4*H*-furo[3,2-*d*][1,3]dioxin-6-yl)methyl acetate (**S6**).**

Prepared according to the general acetylation procedure from alcohol **30** (0.0080 g, 0.050 mmol). Purification by column chromatography (gradient of 0% to 100% EtOAc in hexanes) afforded **S6** as a clear oil (0.0074 g, 81%).  $R_f = 0.31$  (3:7 EtOAc, hexanes).  $[\alpha]_D^{22} = -29.2$  ( $c = 0.27$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.11 (d,  $J = 6.3$  Hz, 1H), 4.63 (d,  $J = 6.3$  Hz, 1H), 4.44-4.38 (m, 2H), 4.21 (app dd,  $J = 11.8$ , 3.6 Hz, 1H), 4.07 (app dd,  $J = 11.8$ , 6.1 Hz, 1H), 3.64 (t,  $J = 9.6$  Hz, 1H), 3.41-3.33 (m, 2H), 2.18-2.06 (m, 5H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 94.3, 79.7, 74.8, 74.3, 71.7, 66.6, 31.1, 21.1. FTIR (thin film) 2921, 2854, 1738, 1458, 1387, 1231, 1165, 1126, 1042, 987, 901  $\text{cm}^{-1}$ . HRMS (ESI) Calcd for  $\text{C}_9\text{H}_{14}\text{O}_5$  ( $\text{M}+\text{Na}$ ) $^+$ : 225.0733, found 225.0739.

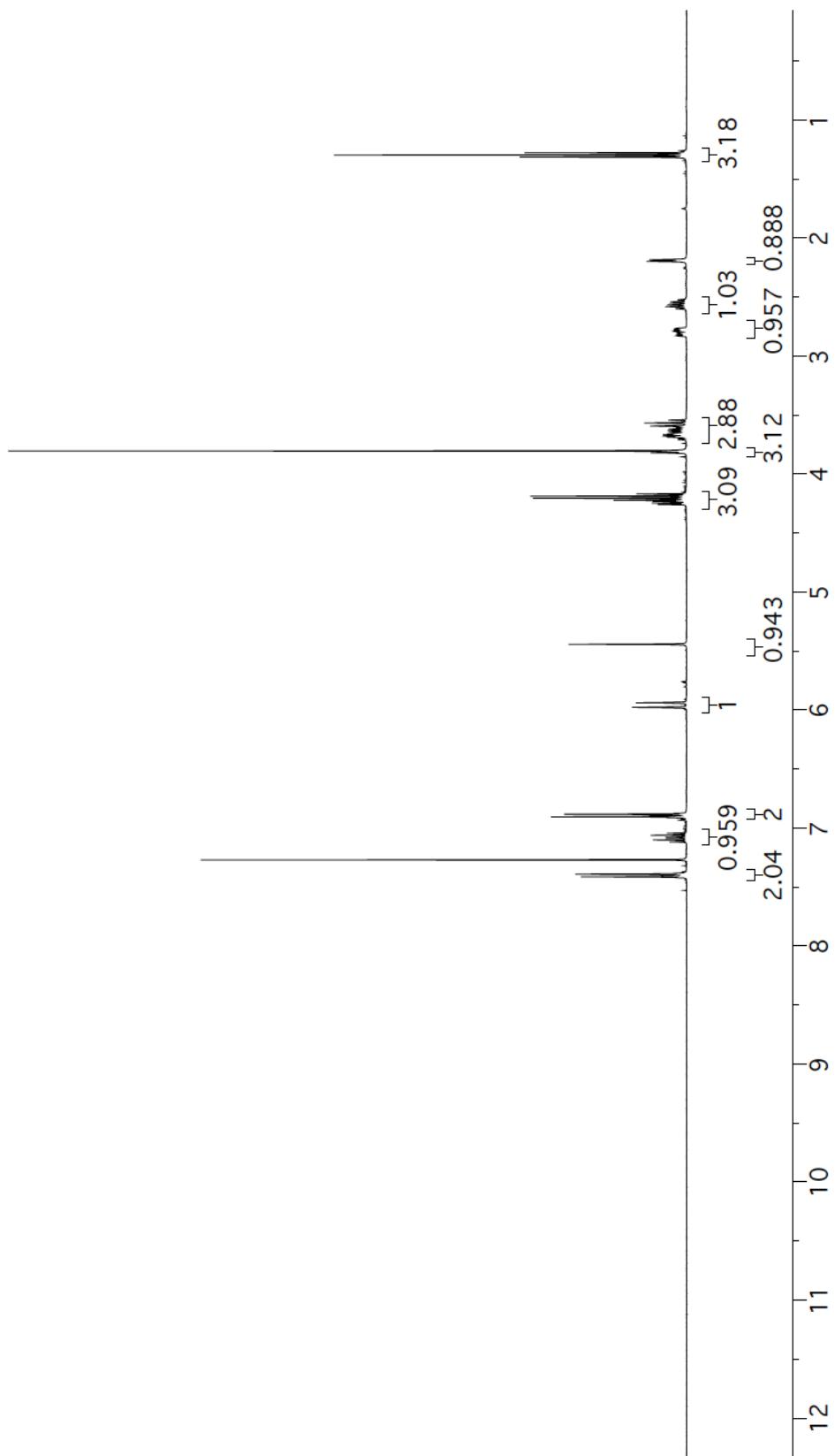
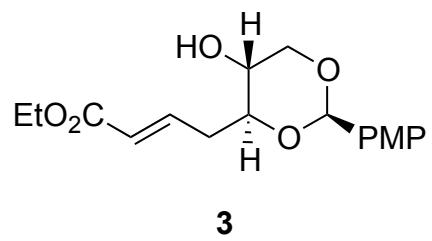


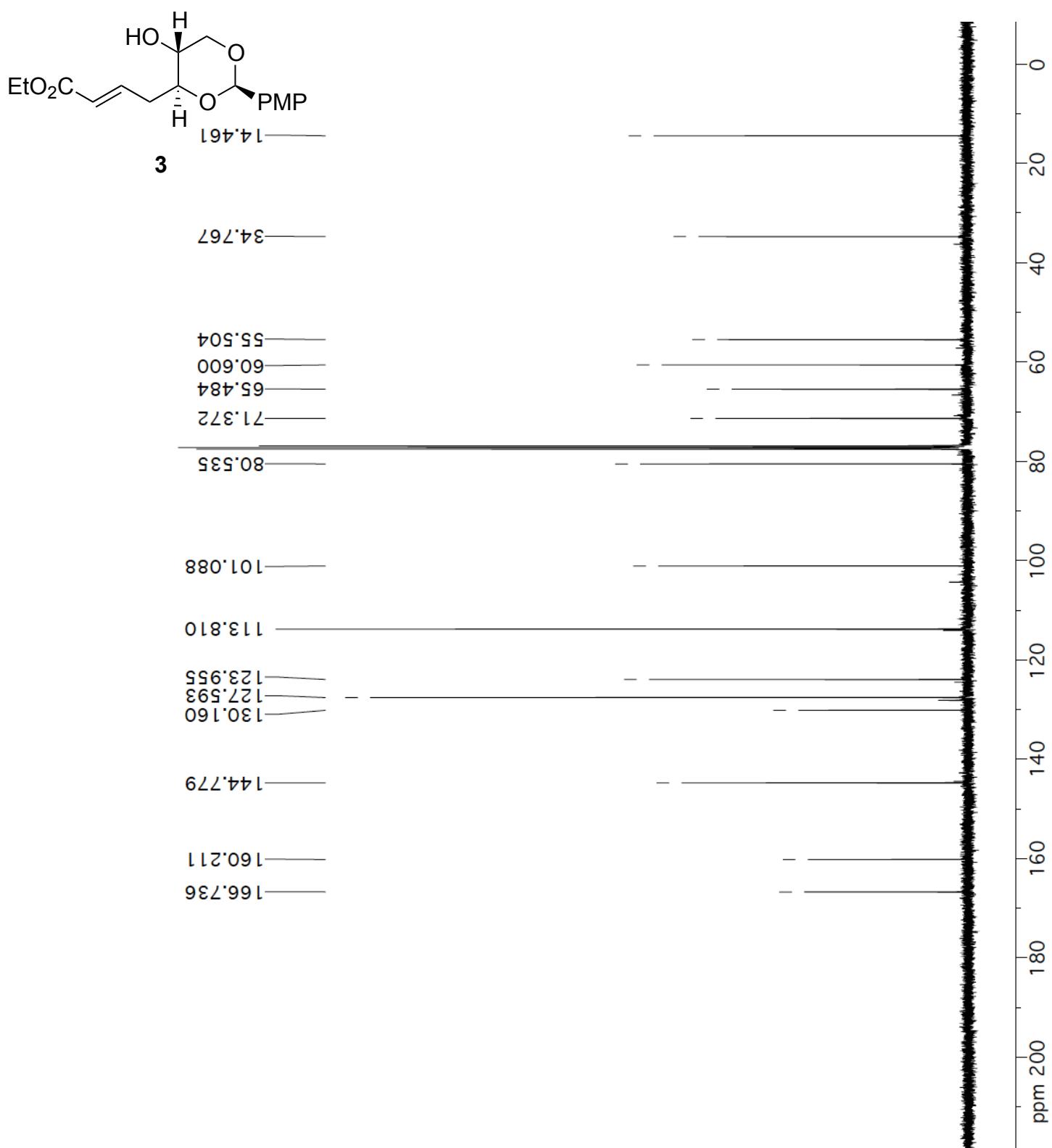
**(4a*R*,5*a**S*,7*R*,8*S*,9*a**R*,10*a**S*)-8-methyloctahydro-4*H*-pyranopyrano[2',3':5,6]pyrano[3,2-*d*][1,3]dioxin-7-yl 4-bromobenzoate (**S7**).**

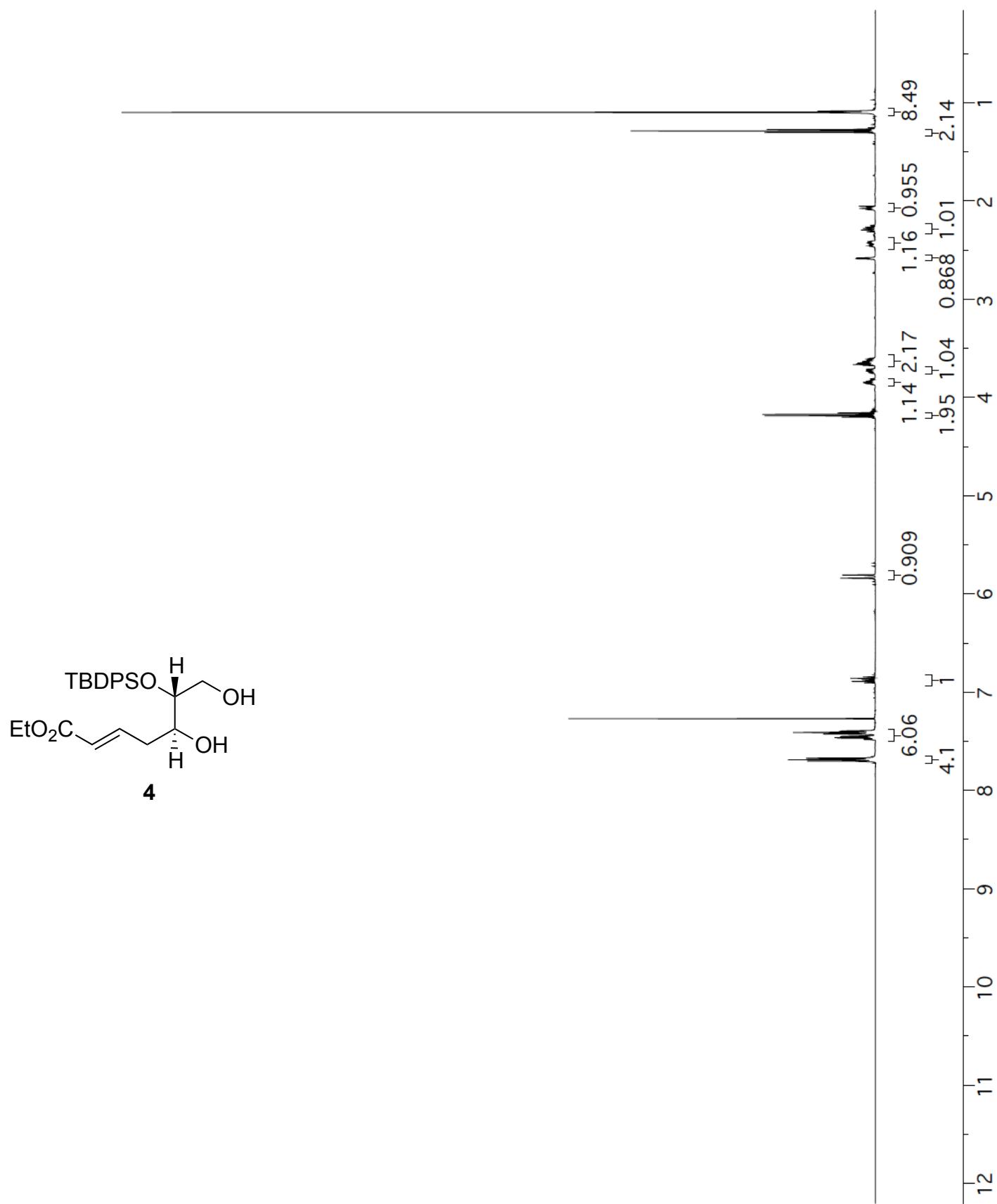
Prepared according to the general acetylation procedure from alcohol **36** (0.015 g, 0.065 mmol) and using *p*-bromobenzoyl chloride (0.044 g, 0.20 mmol) in place of  $\text{Ac}_2\text{O}$ . Purification by column chromatography (gradient of

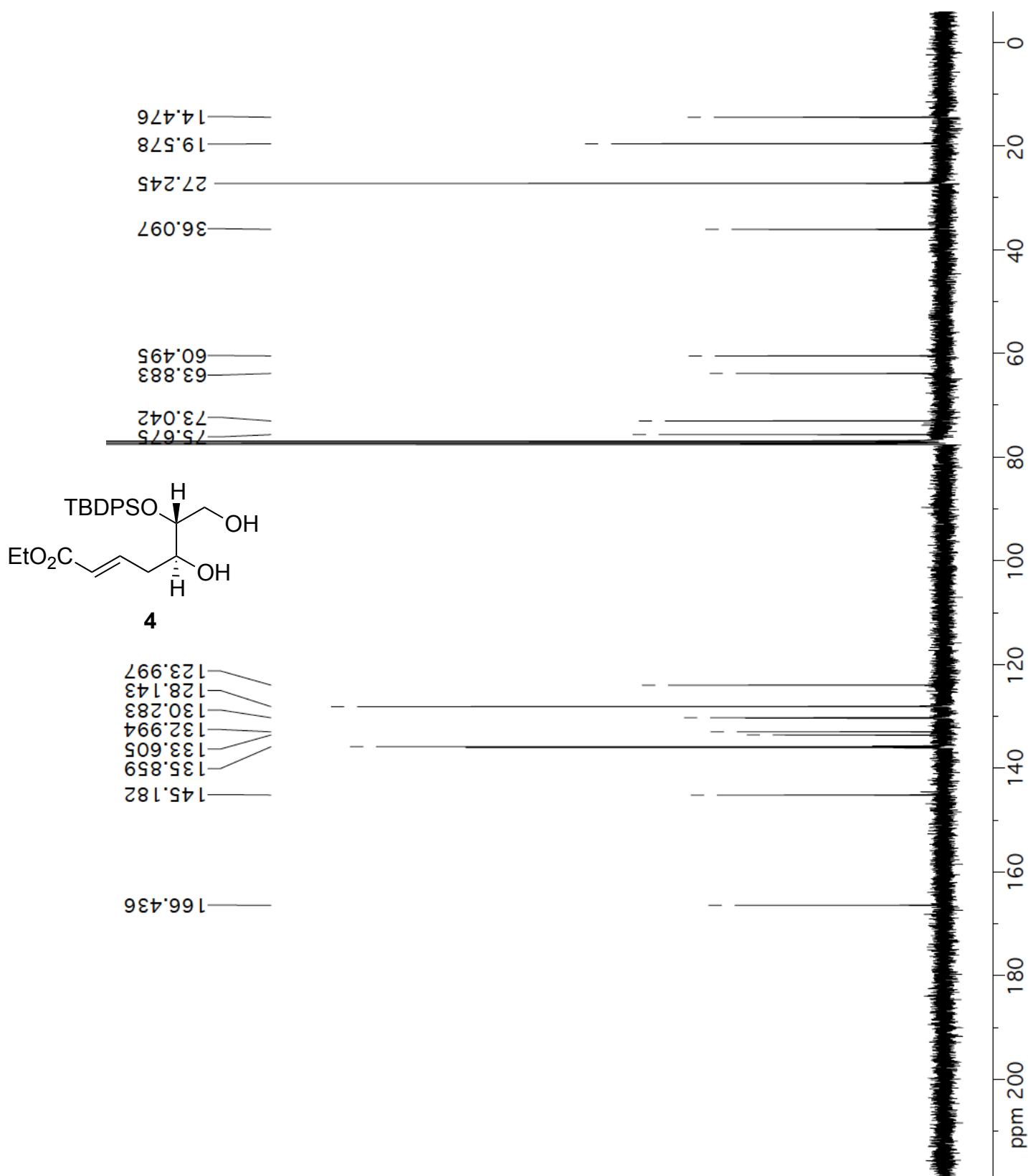
25% to 100% EtOAc in hexanes) afforded **S7** as an amorphous white solid (0.018 g, 67%).  $R_f$  = 0.85 (100% EtOAc).  $[\alpha]_D^{22} = -15.5$  ( $c = 0.88$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 7.1$  Hz, 2H), 7.61 (d,  $J = 7.1$  Hz, 2H), 5.03 (d,  $J = 6.2$  Hz, 1H), 4.80 (app ddd,  $J = 11.2, 9.5, 4.8$  Hz, 1H), 4.63 (d,  $J = 6.3$  Hz, 1H), 4.19 (app dd,  $J = 10.3, 3.8$  Hz, 1H), 3.61-3.58 (m, 1H), 3.43 (t,  $J = 10.1$  Hz, 1H), 3.35-3.19 (m, 4H), 2.56 (app dt,  $J = 11.4, 4.4$  Hz, 1H), 2.42 (app dt,  $J = 11.4, 3.8$  Hz, 1H), 1.69 (q,  $J = 11.3$  Hz, 1H), 1.59 (q,  $J = 11.4$  Hz, 1H), 1.25 (d,  $J = 6.2$ , 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 132.1, 131.4, 129.0, 128.7, 94.0, 77.2, 76.9, 76.6, 76.2, 74.0, 73.1, 69.2, 35.2, 35.0, 18.1. FTIR (thin film) 2973, 2938, 2873, 1728, 1591, 1285, 1077  $\text{cm}^{-1}$ . HRMS (ESI) Calcd for  $\text{C}_{18}\text{H}_{21}\text{BrO}_6$  ( $\text{M}+\text{H}$ ) $^+$ : 413.0600, found 413.0594.

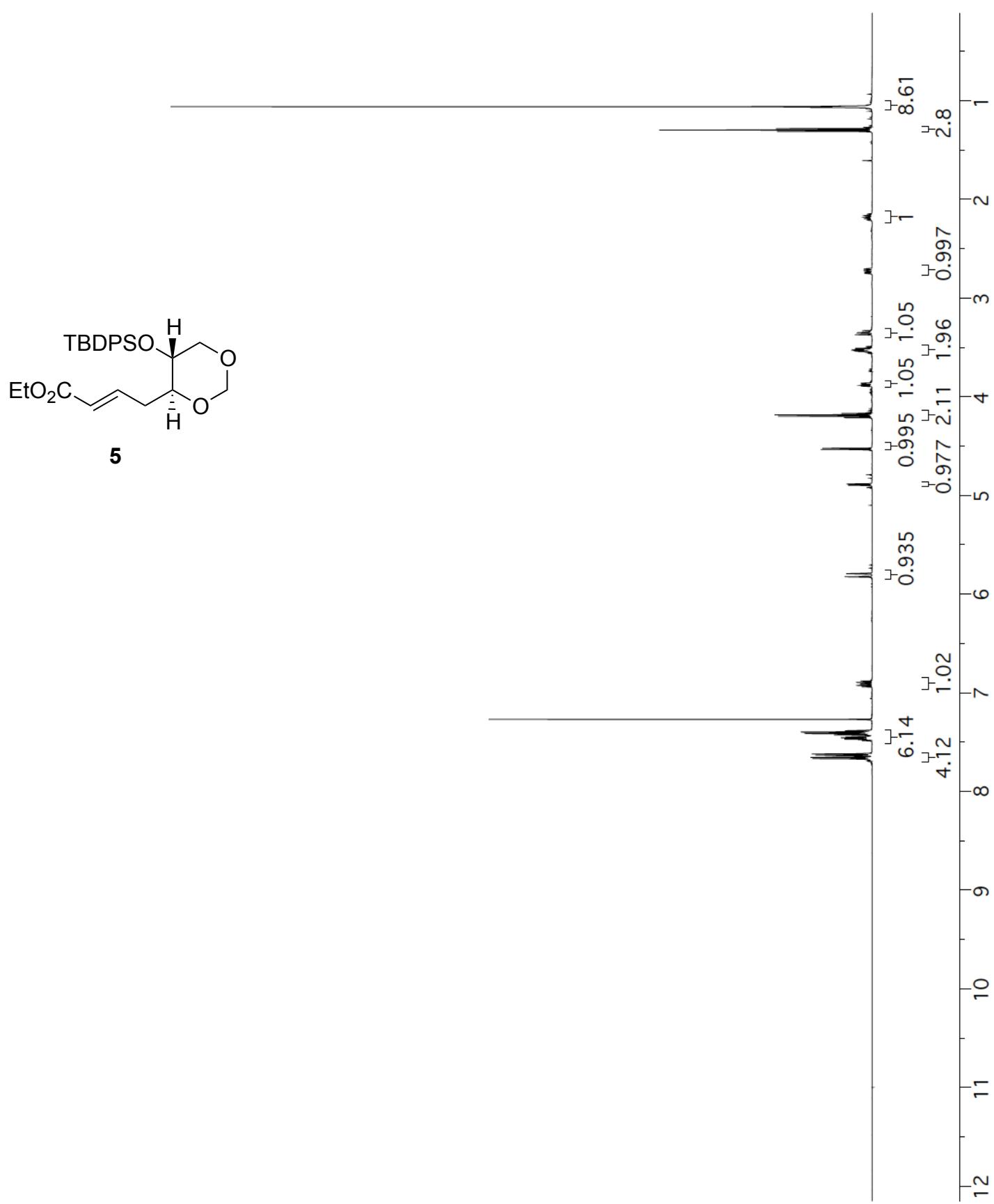
**$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra**

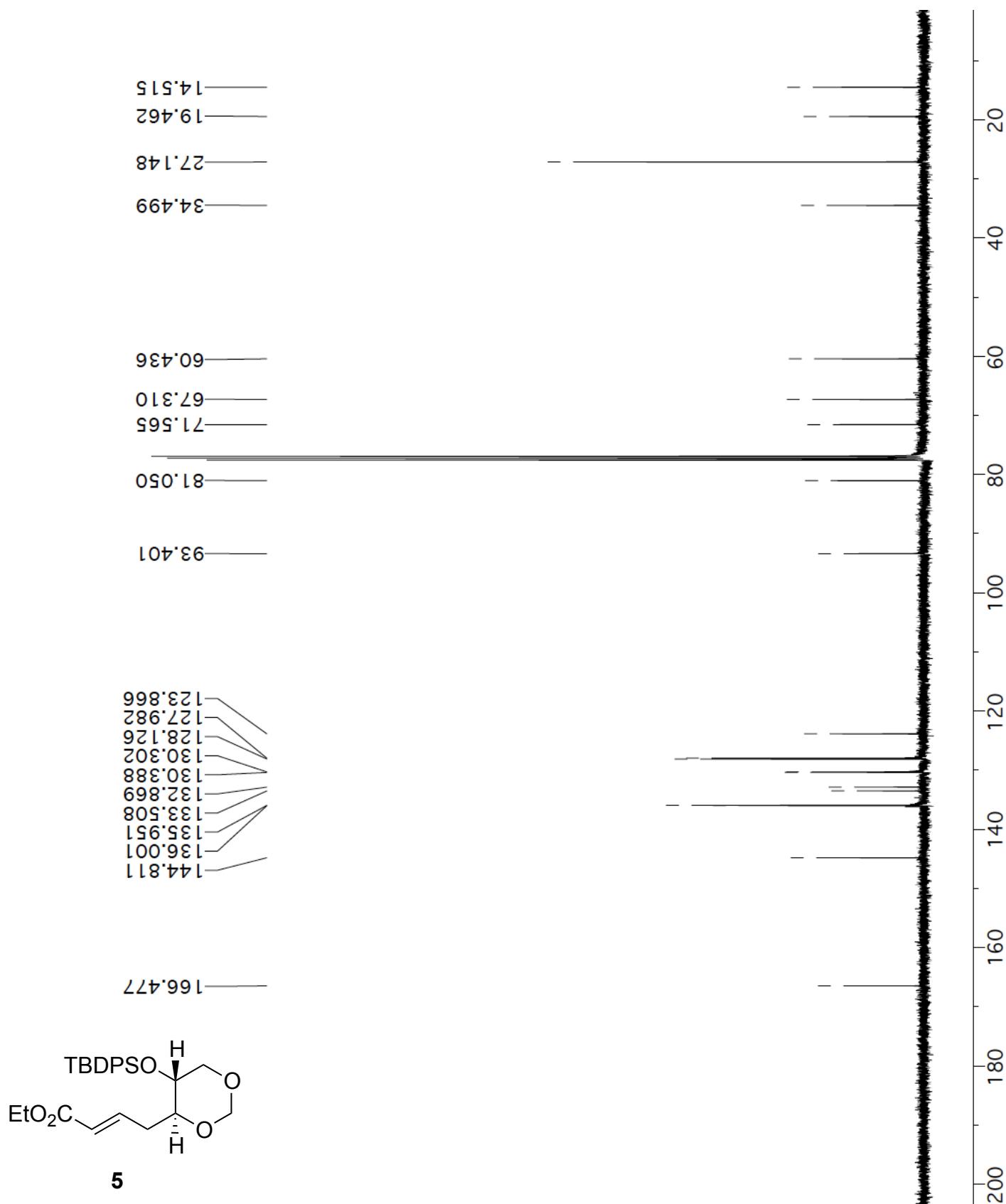


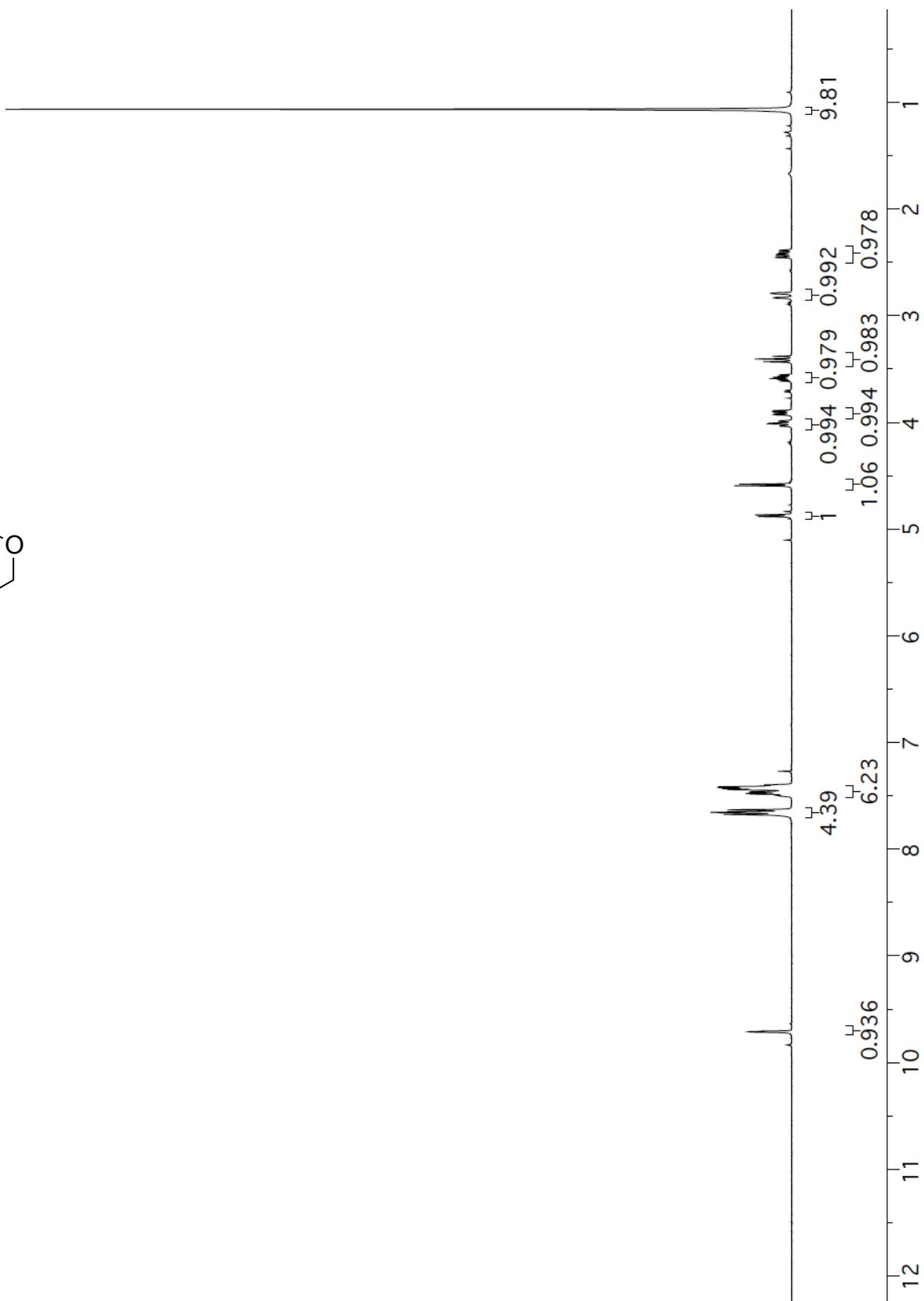
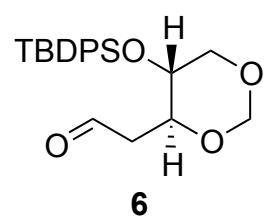


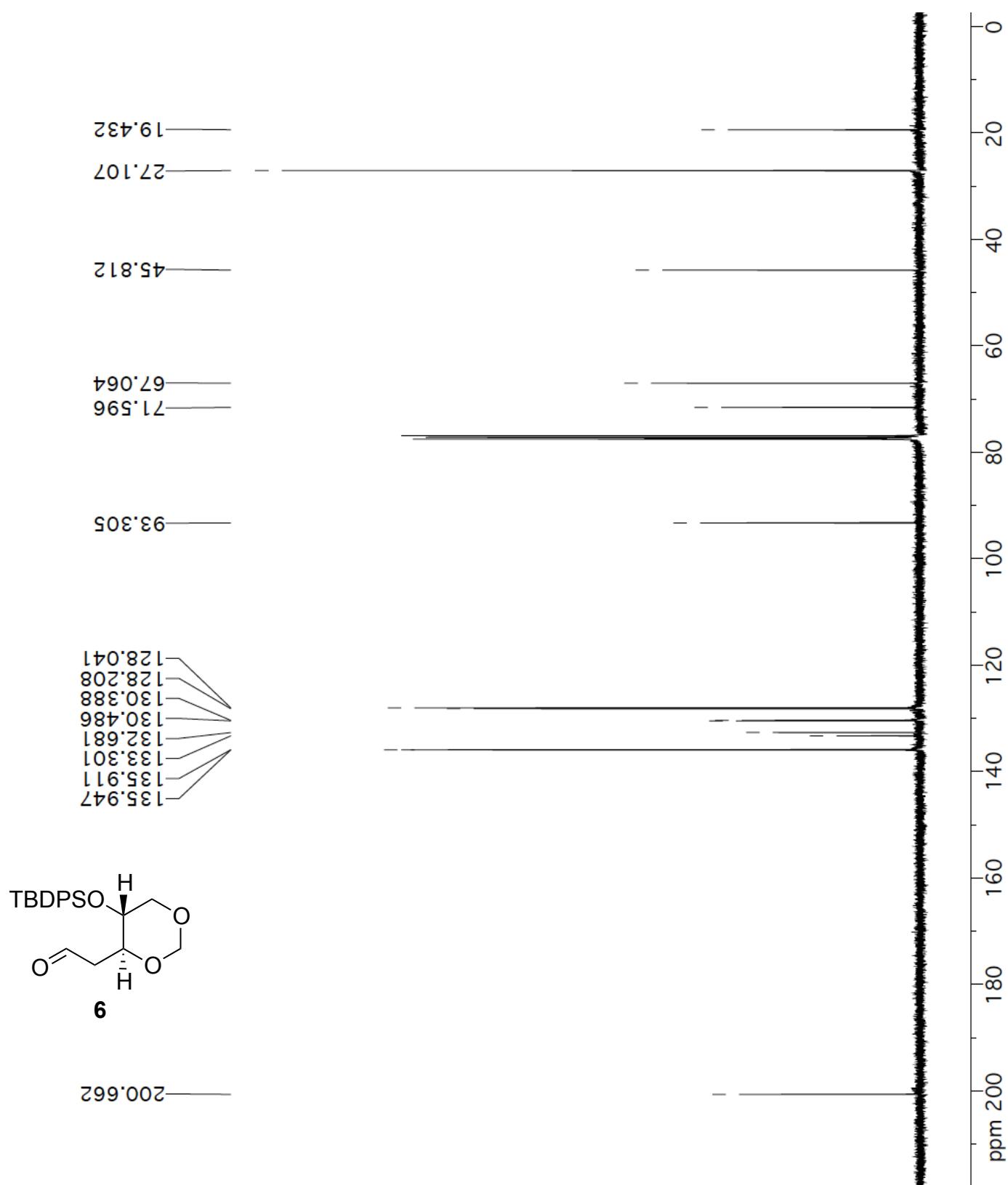


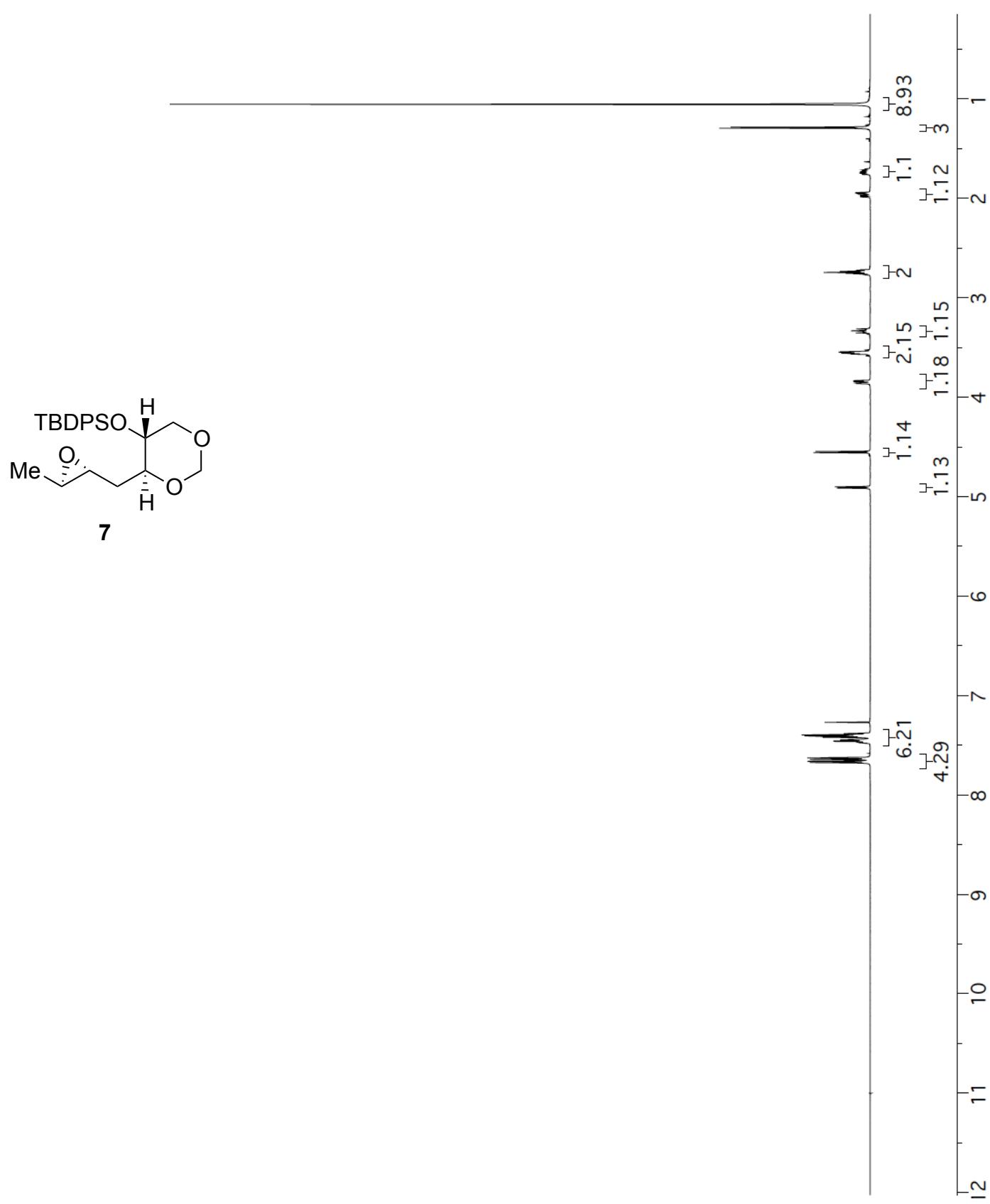


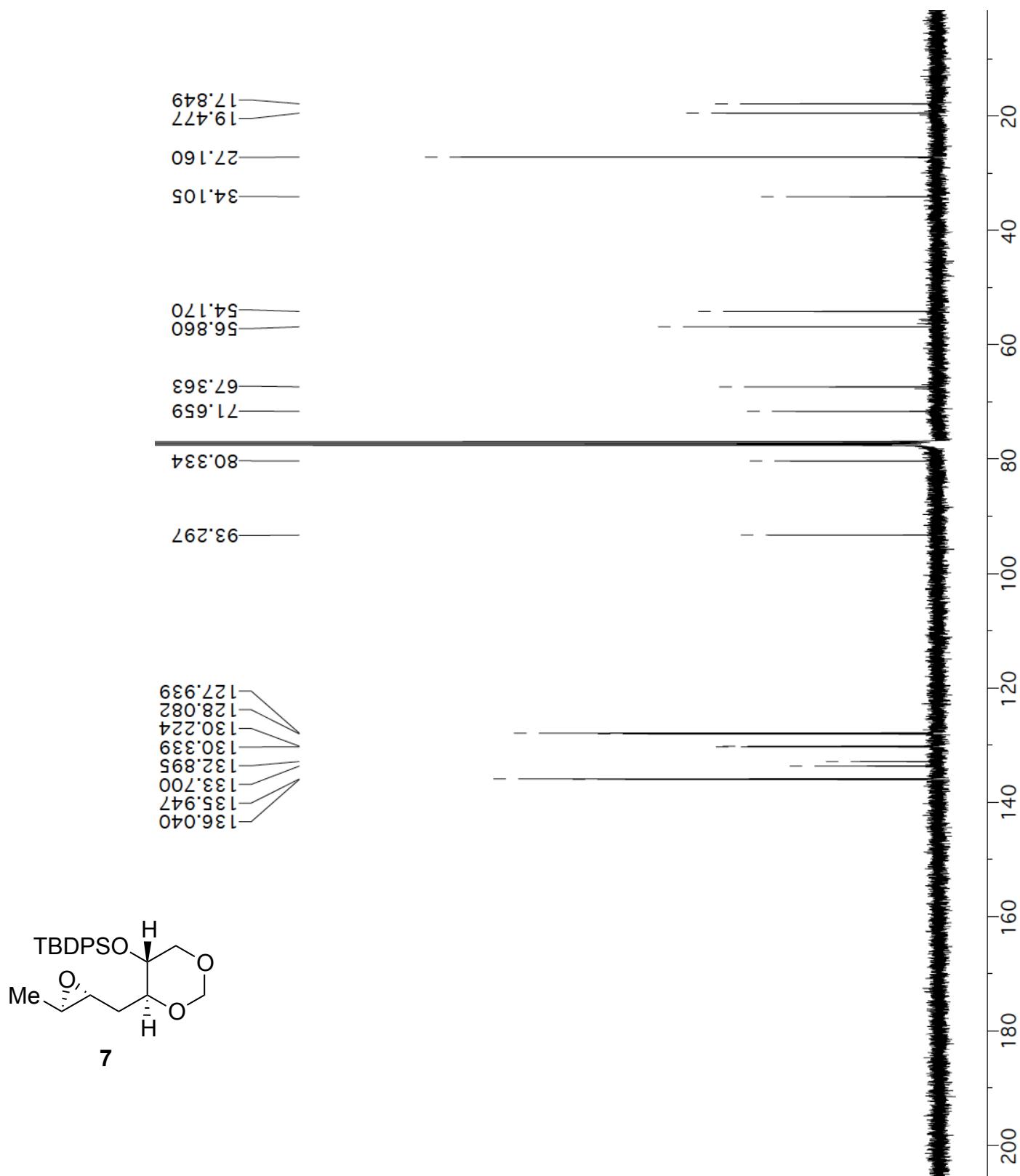


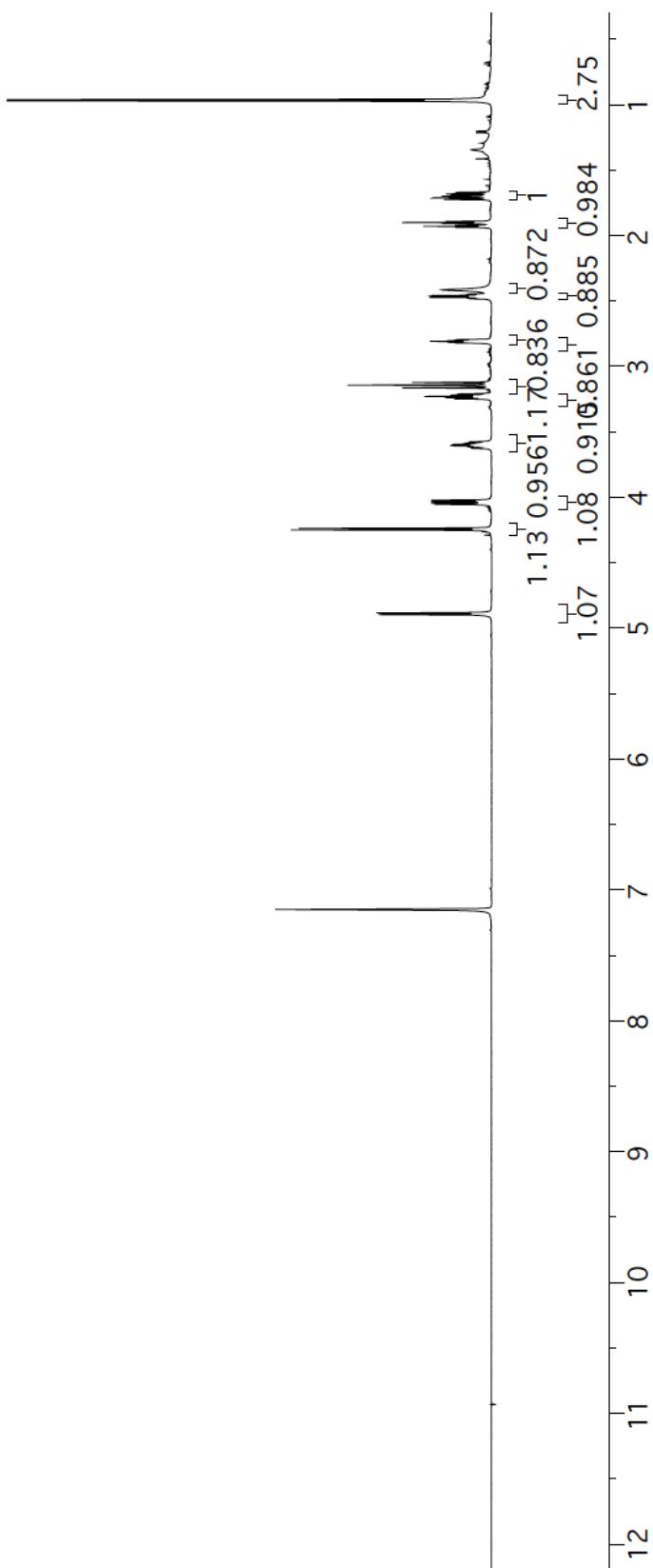
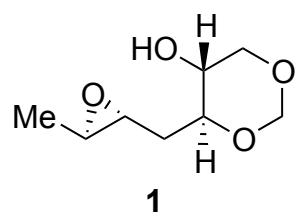


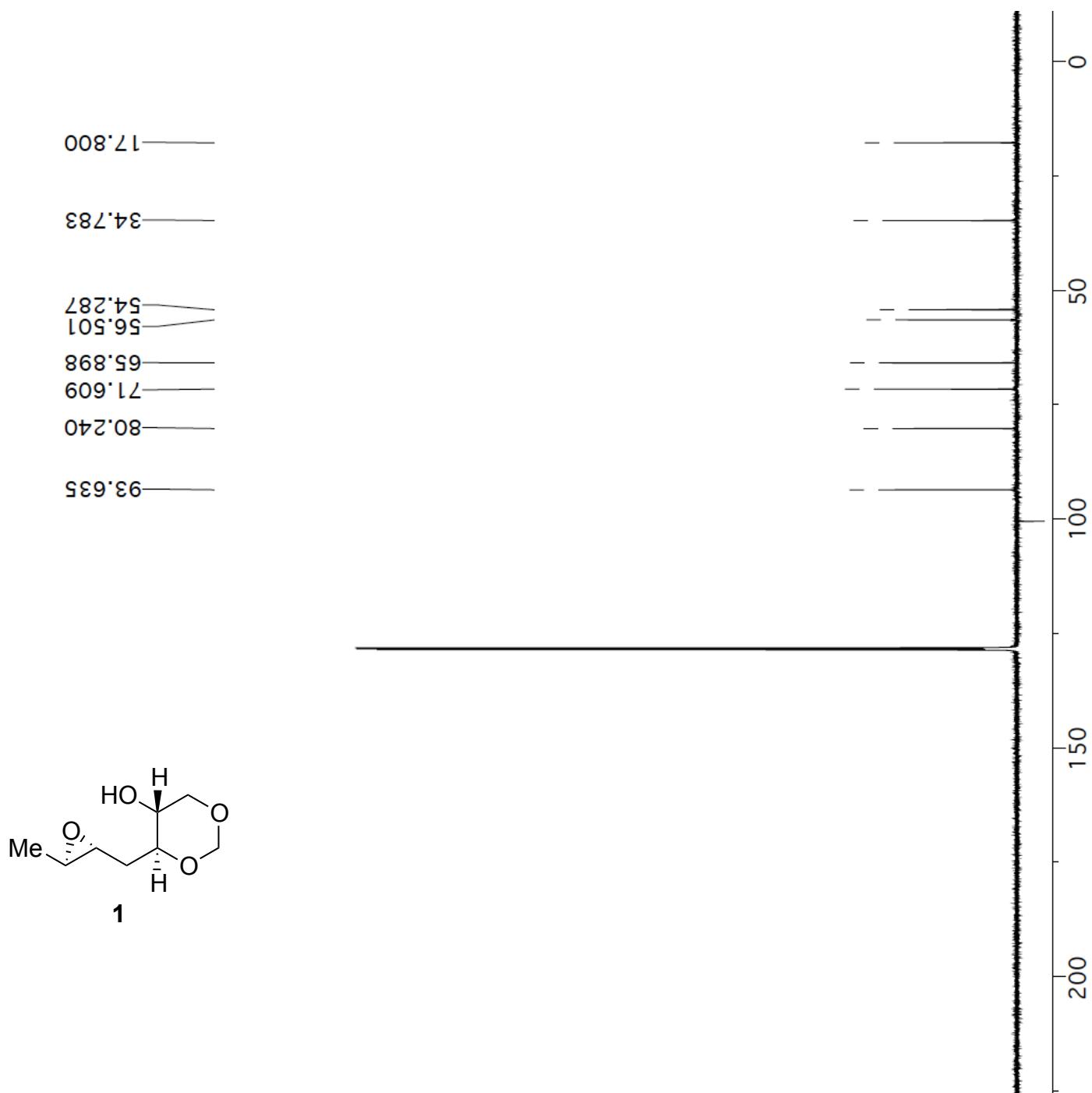


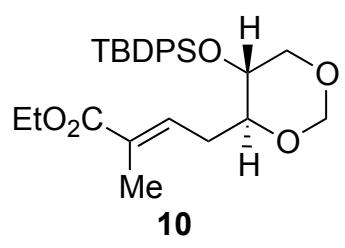
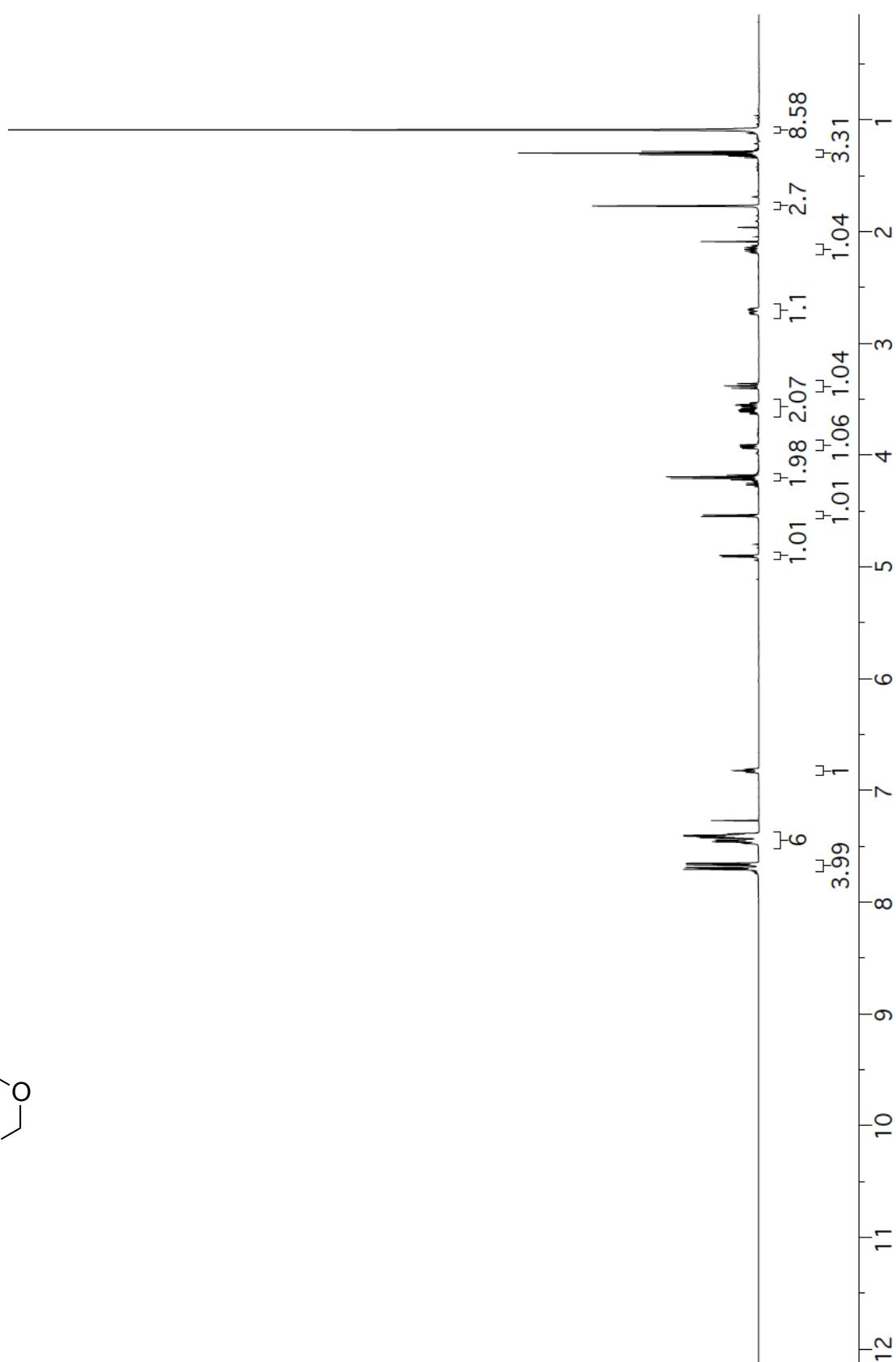


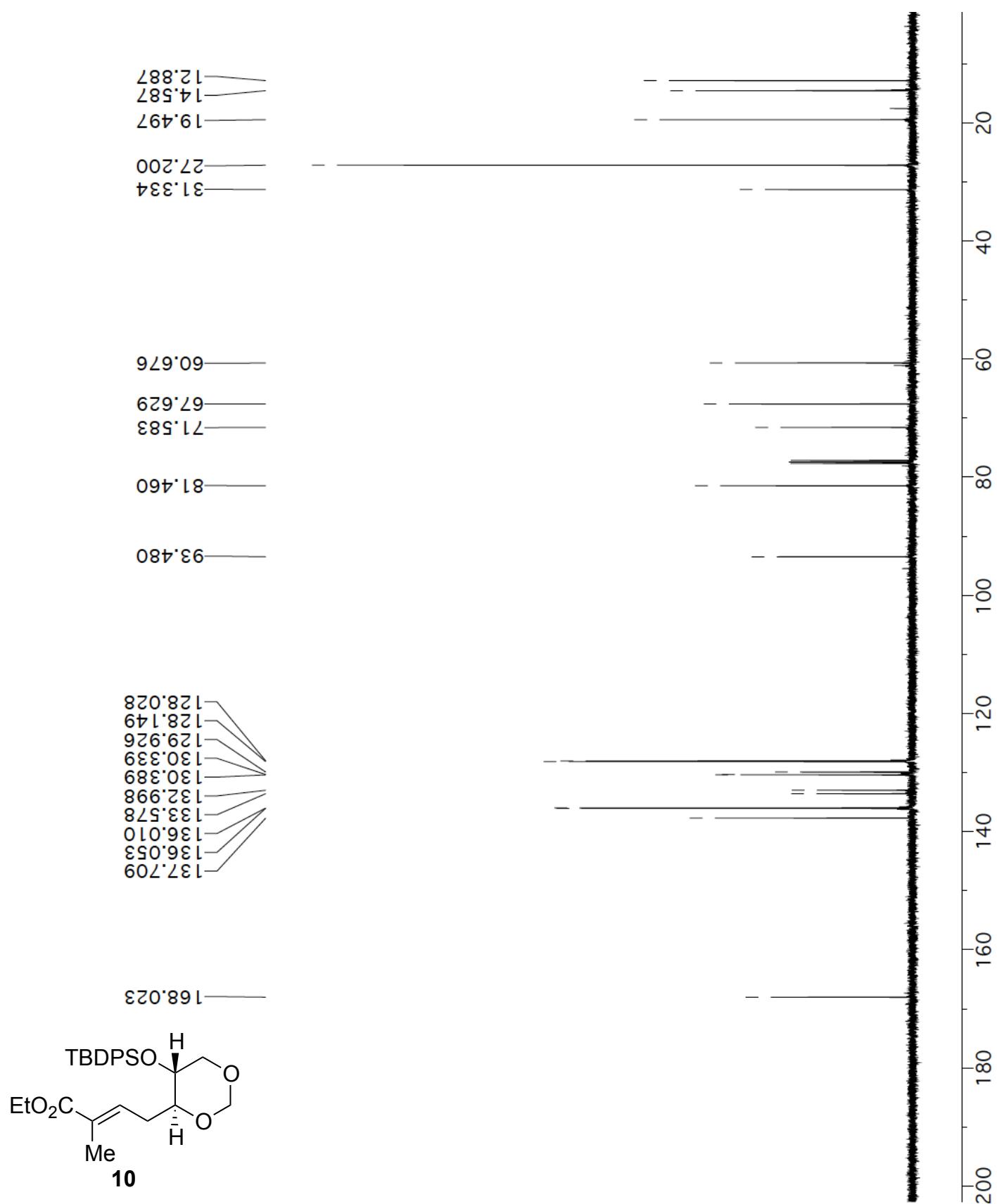


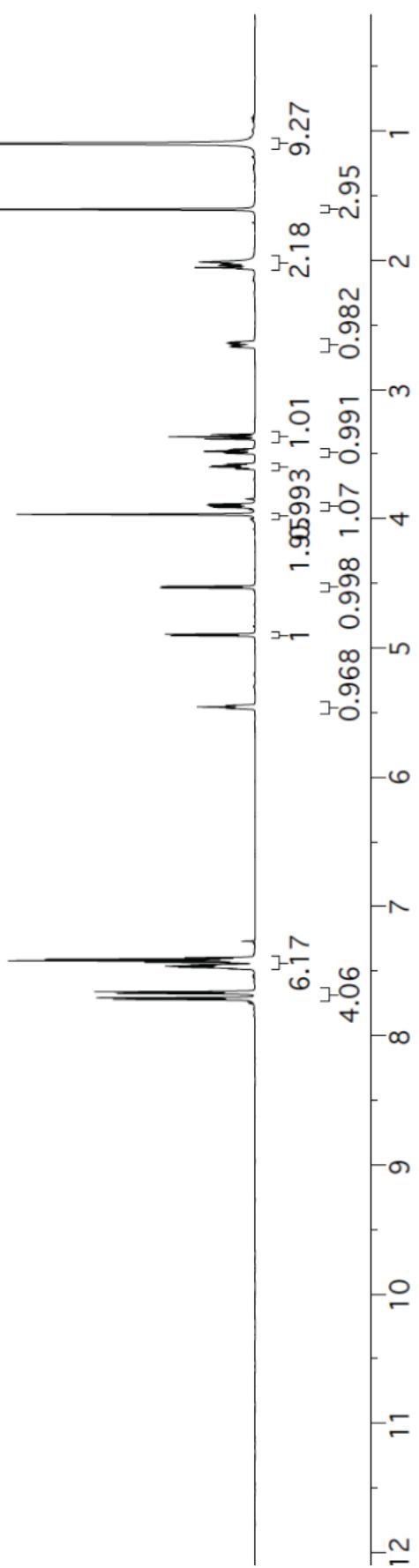
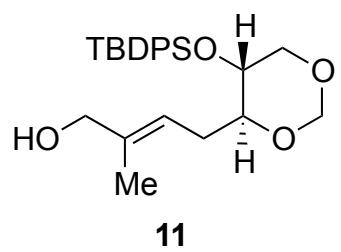


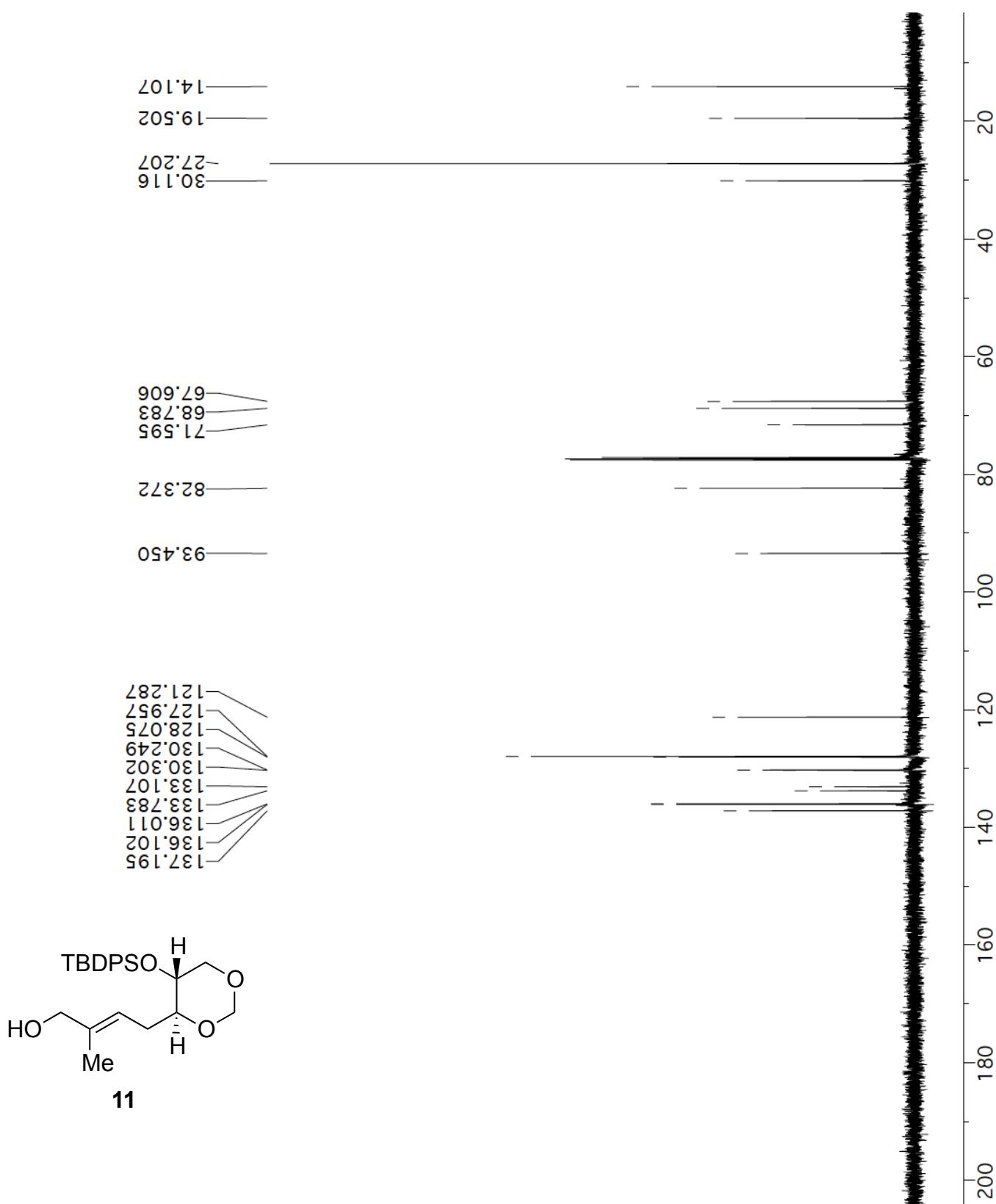


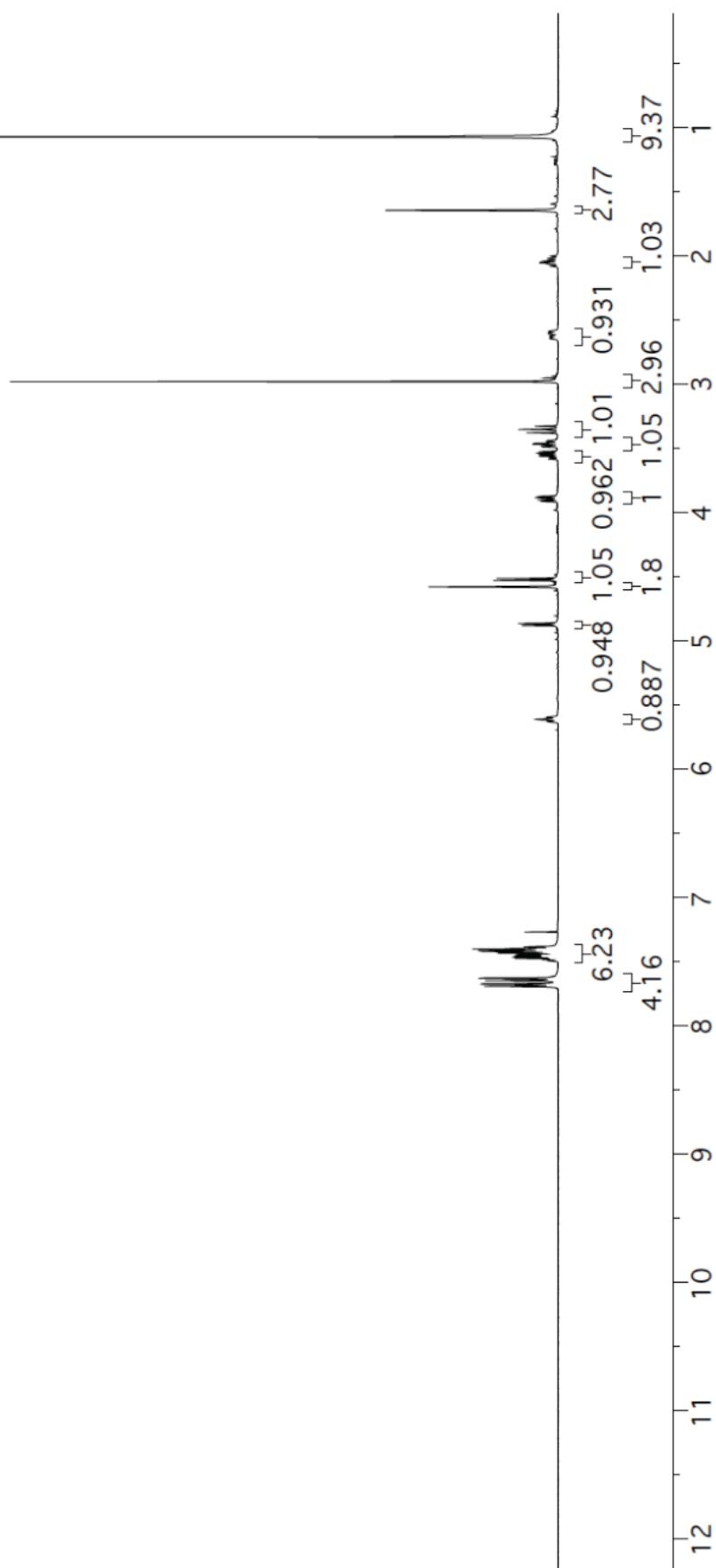
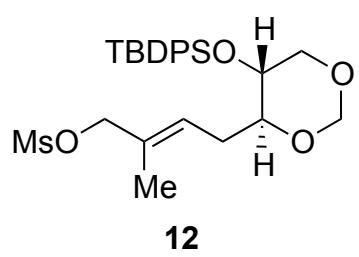


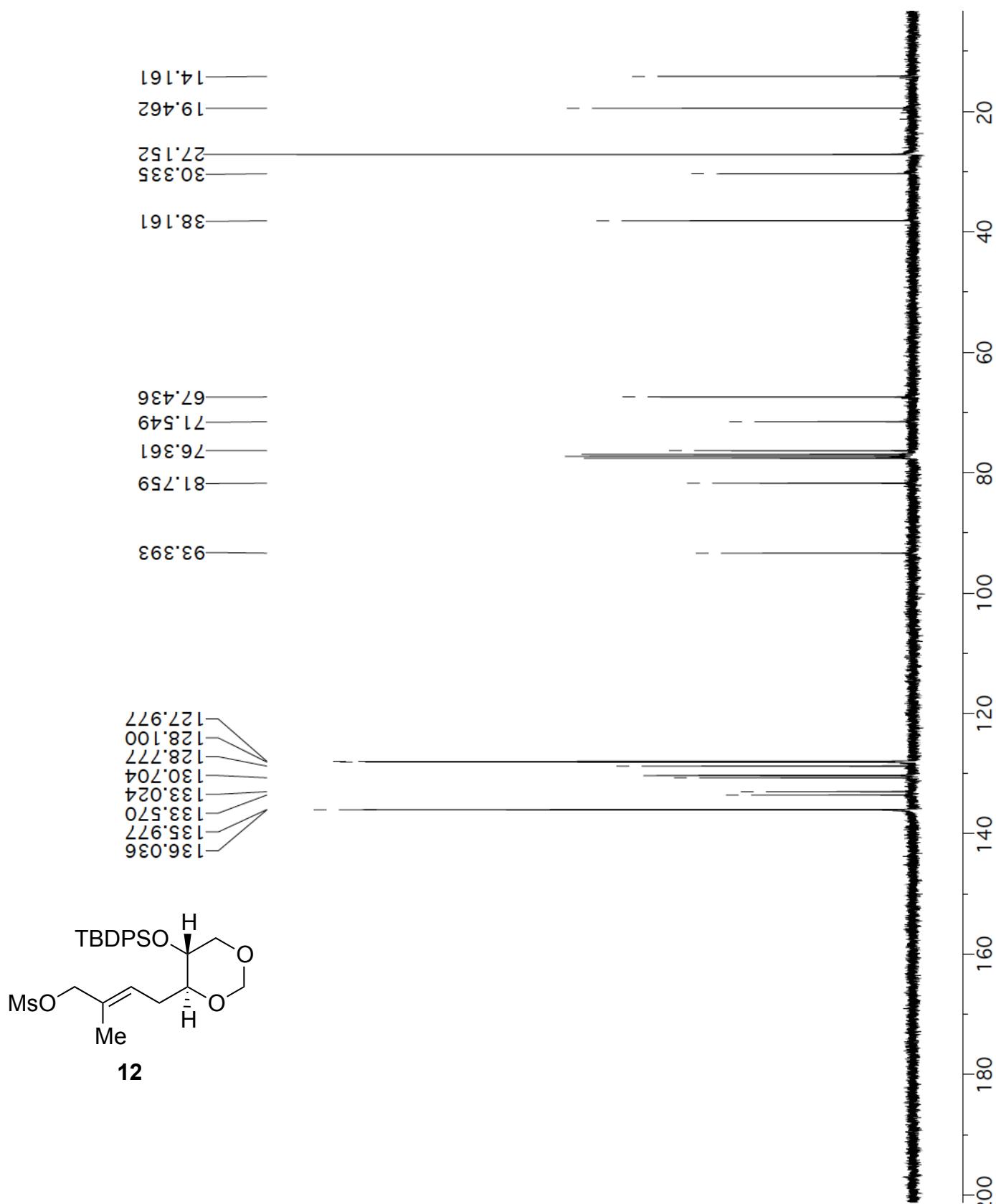


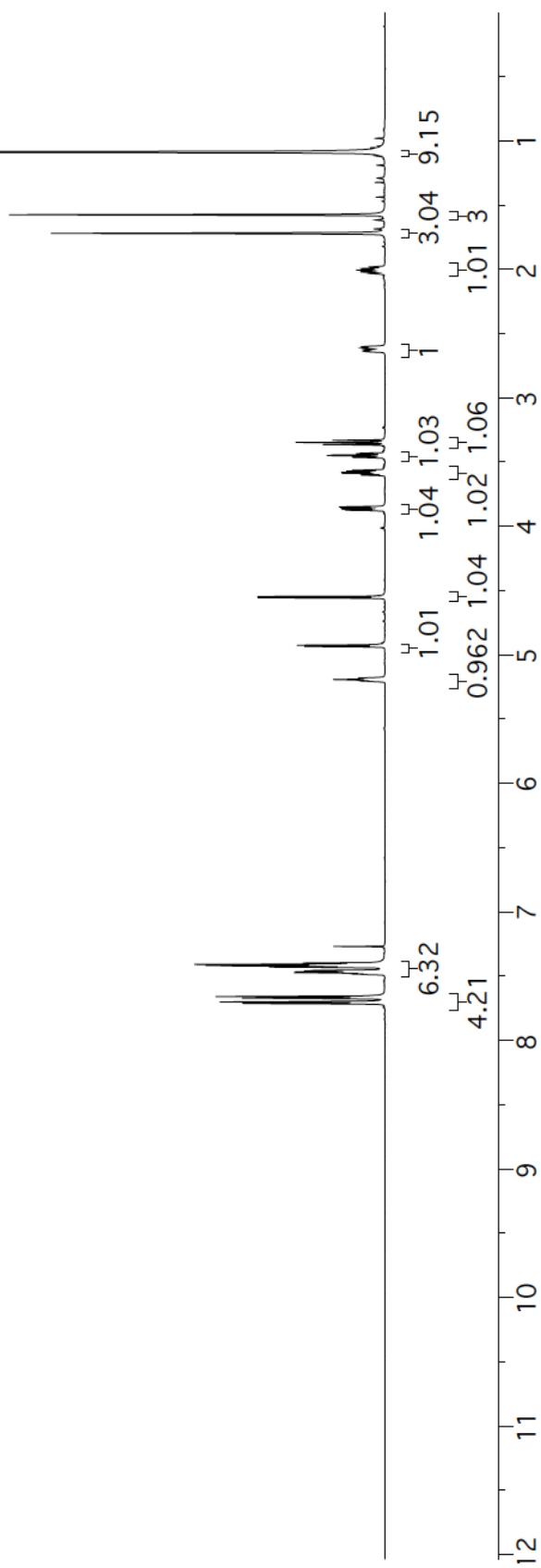
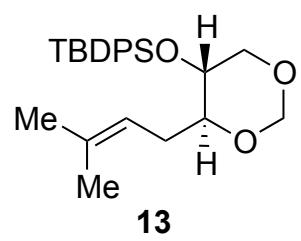


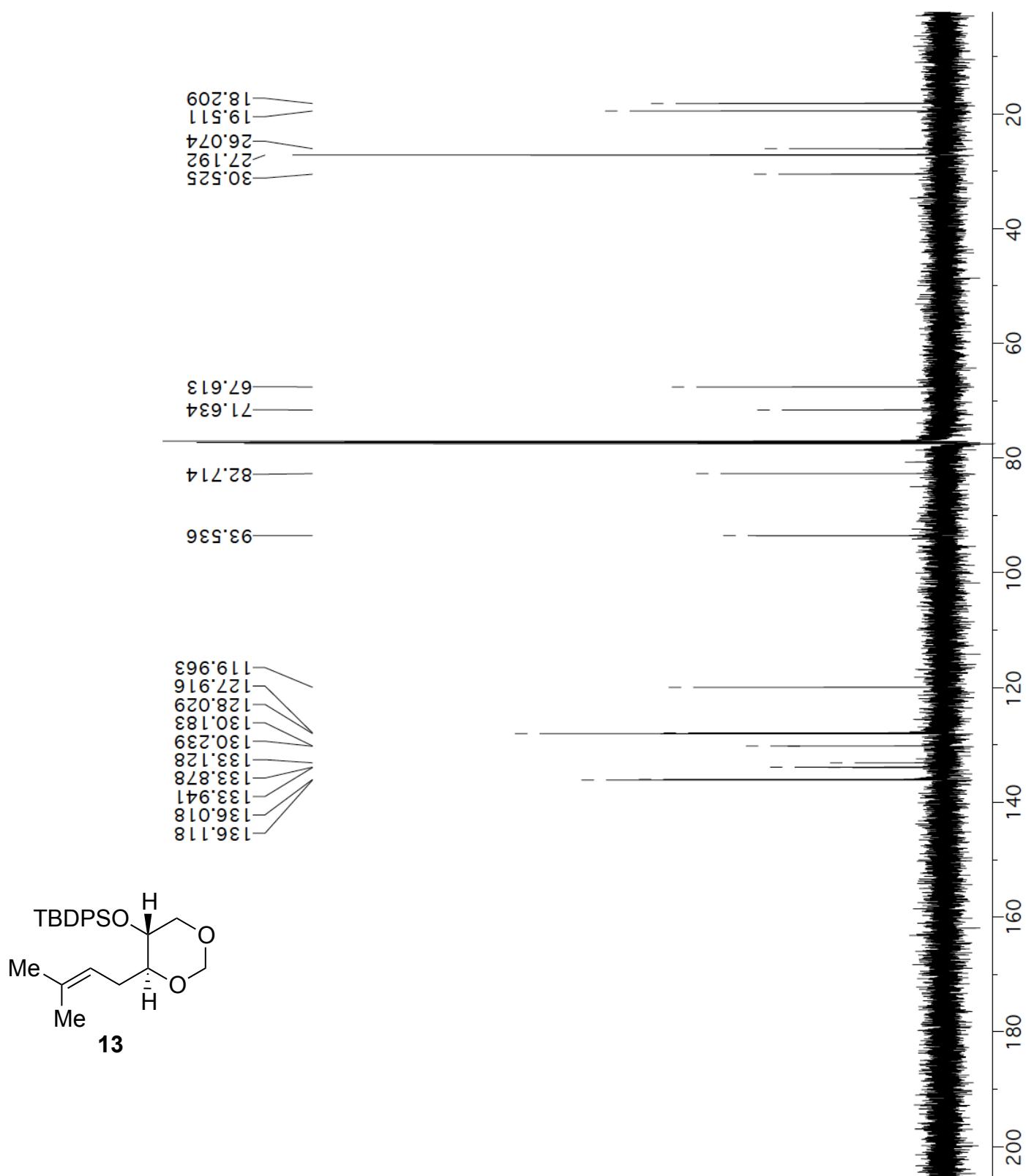


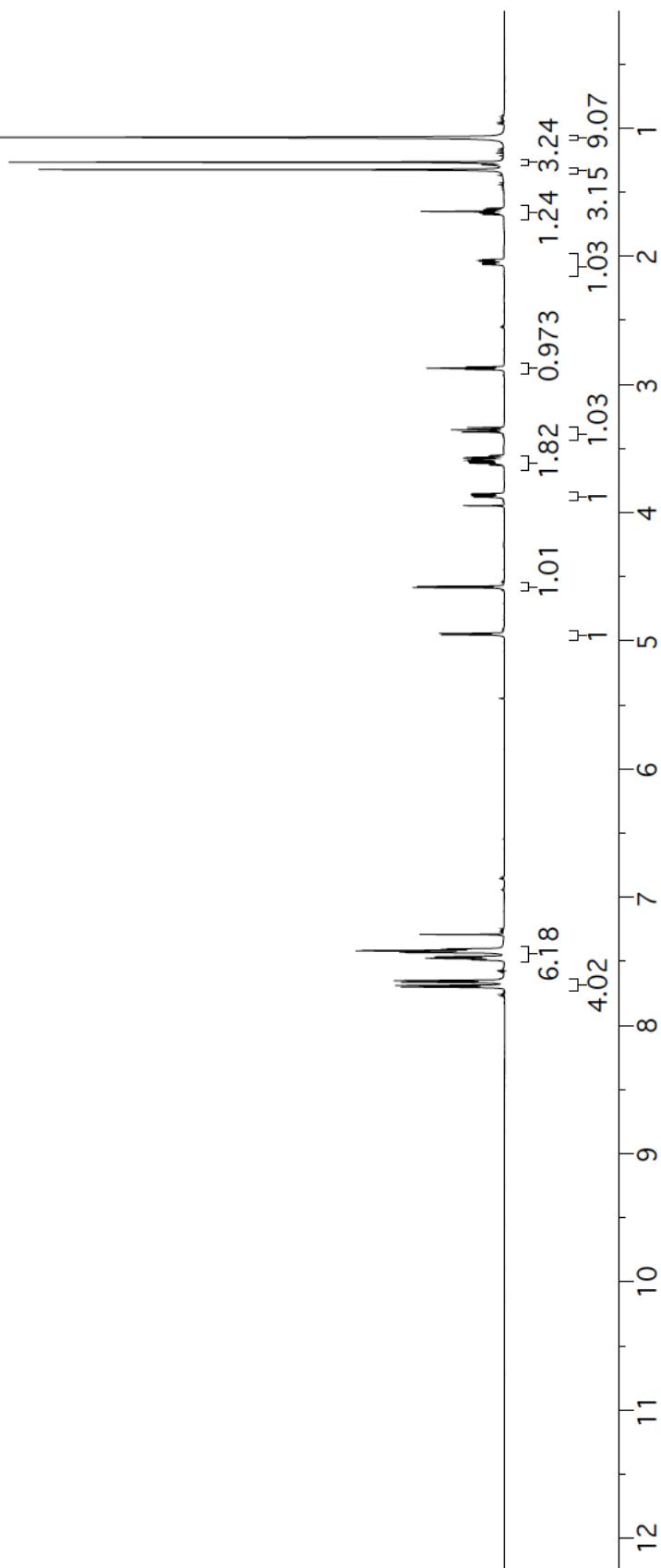
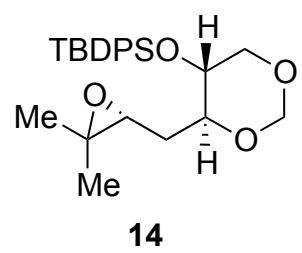


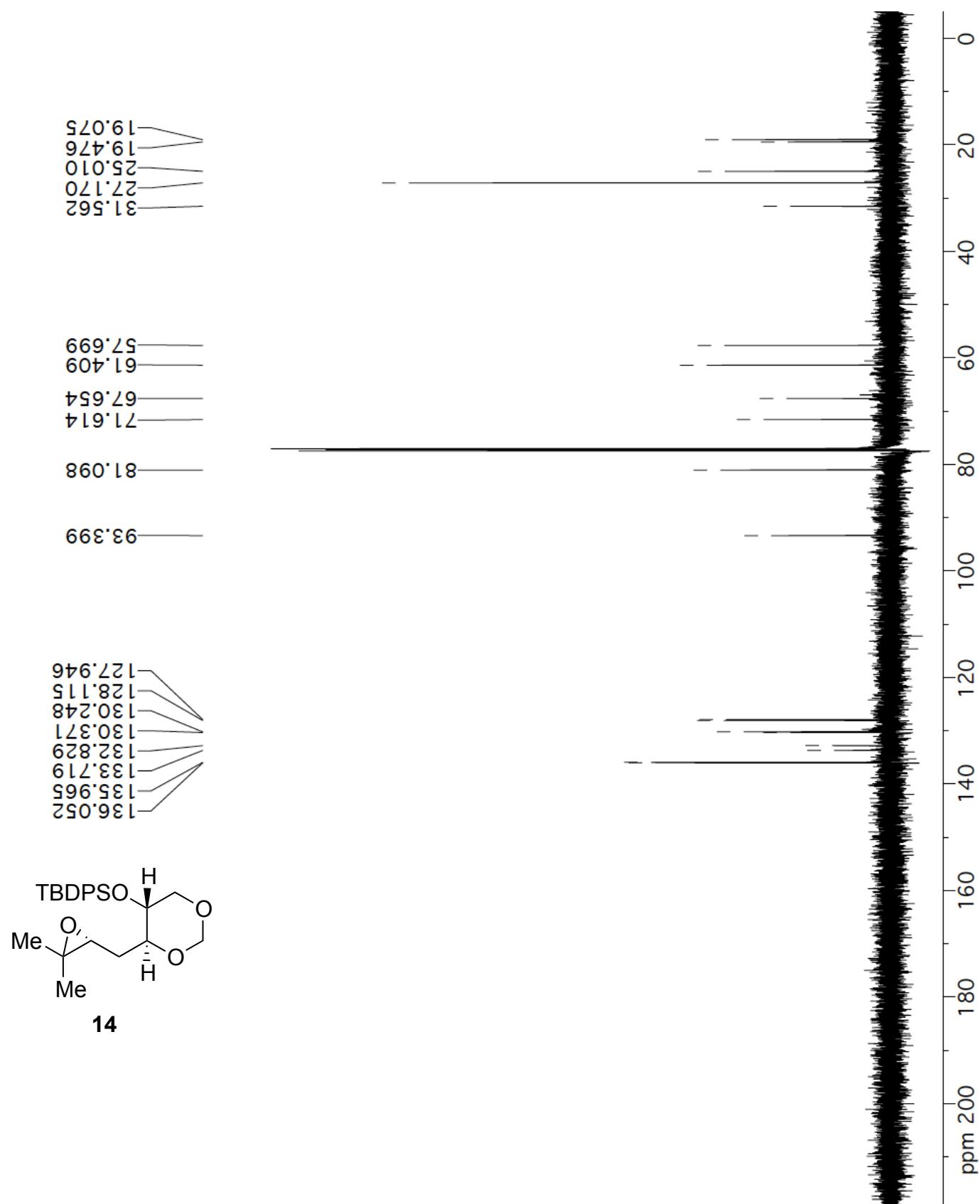


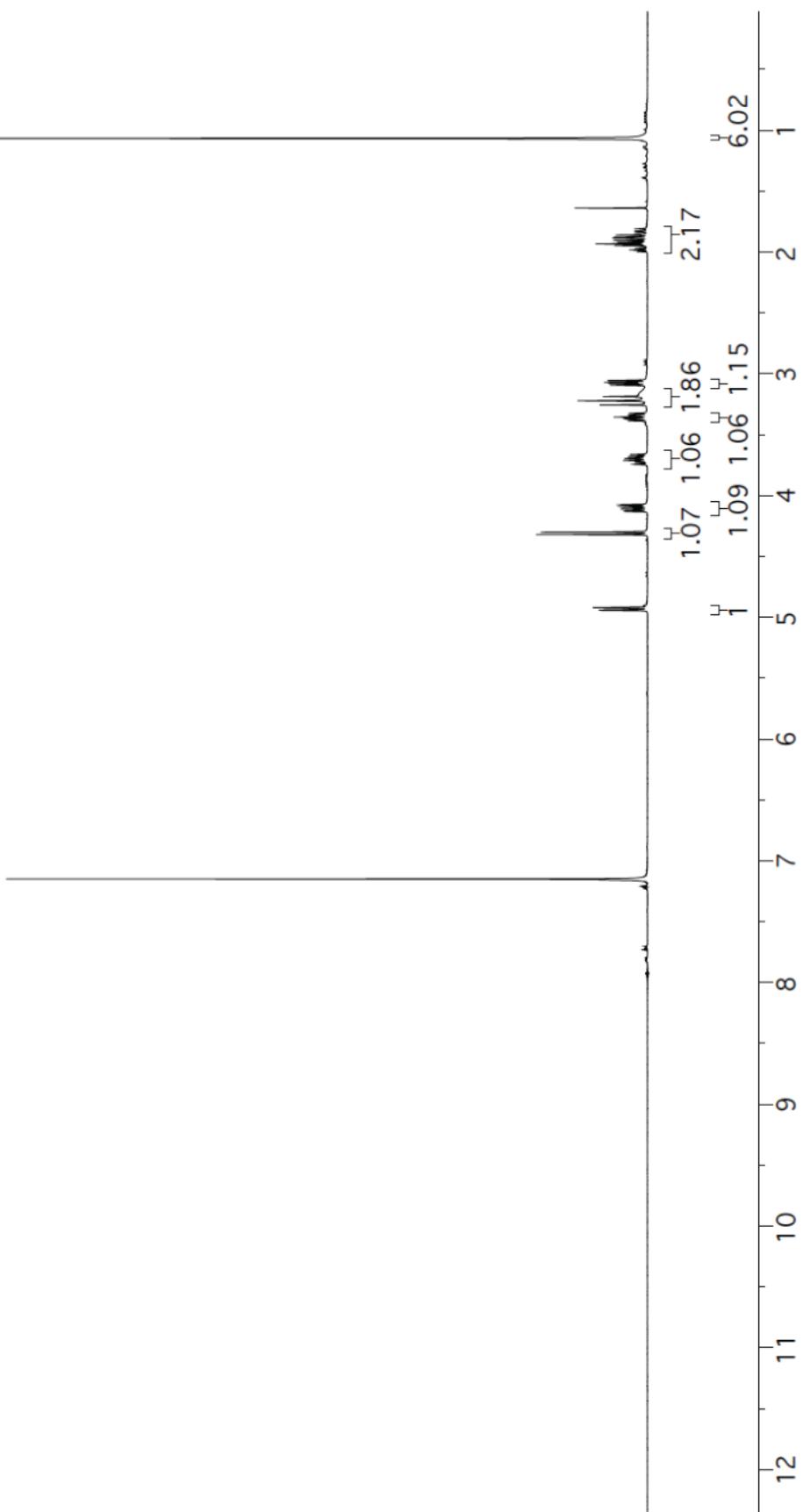
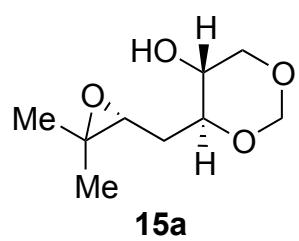


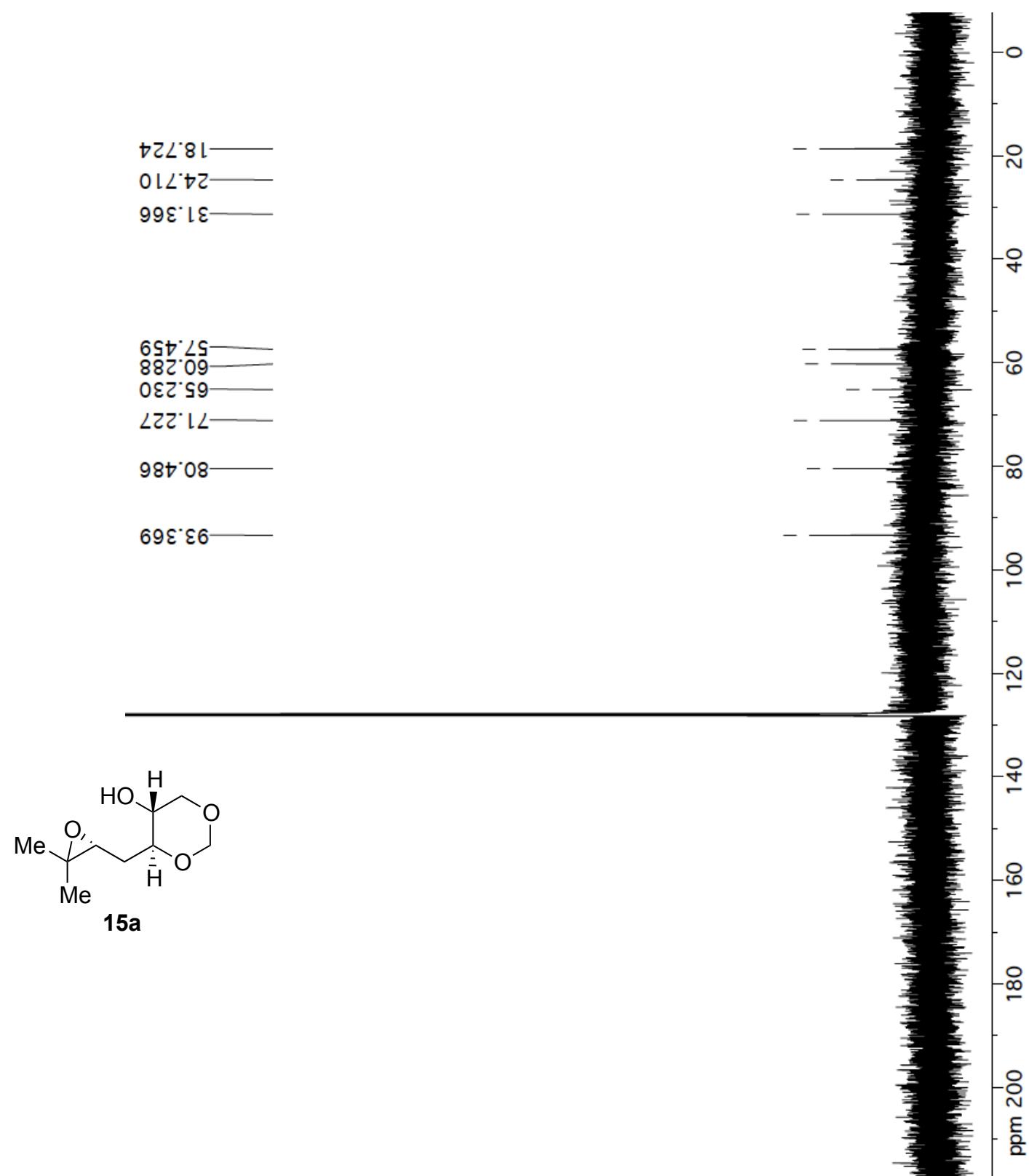


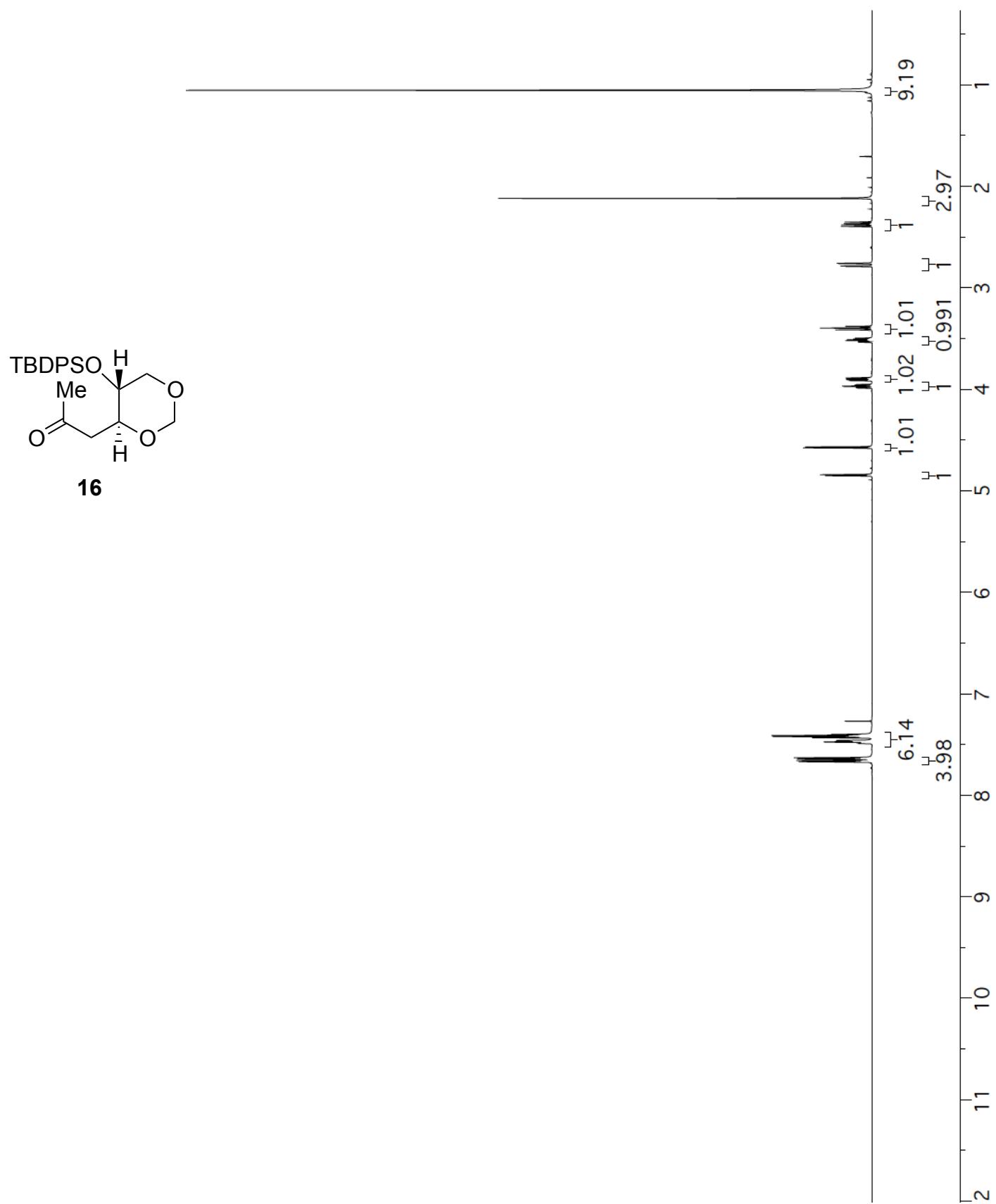


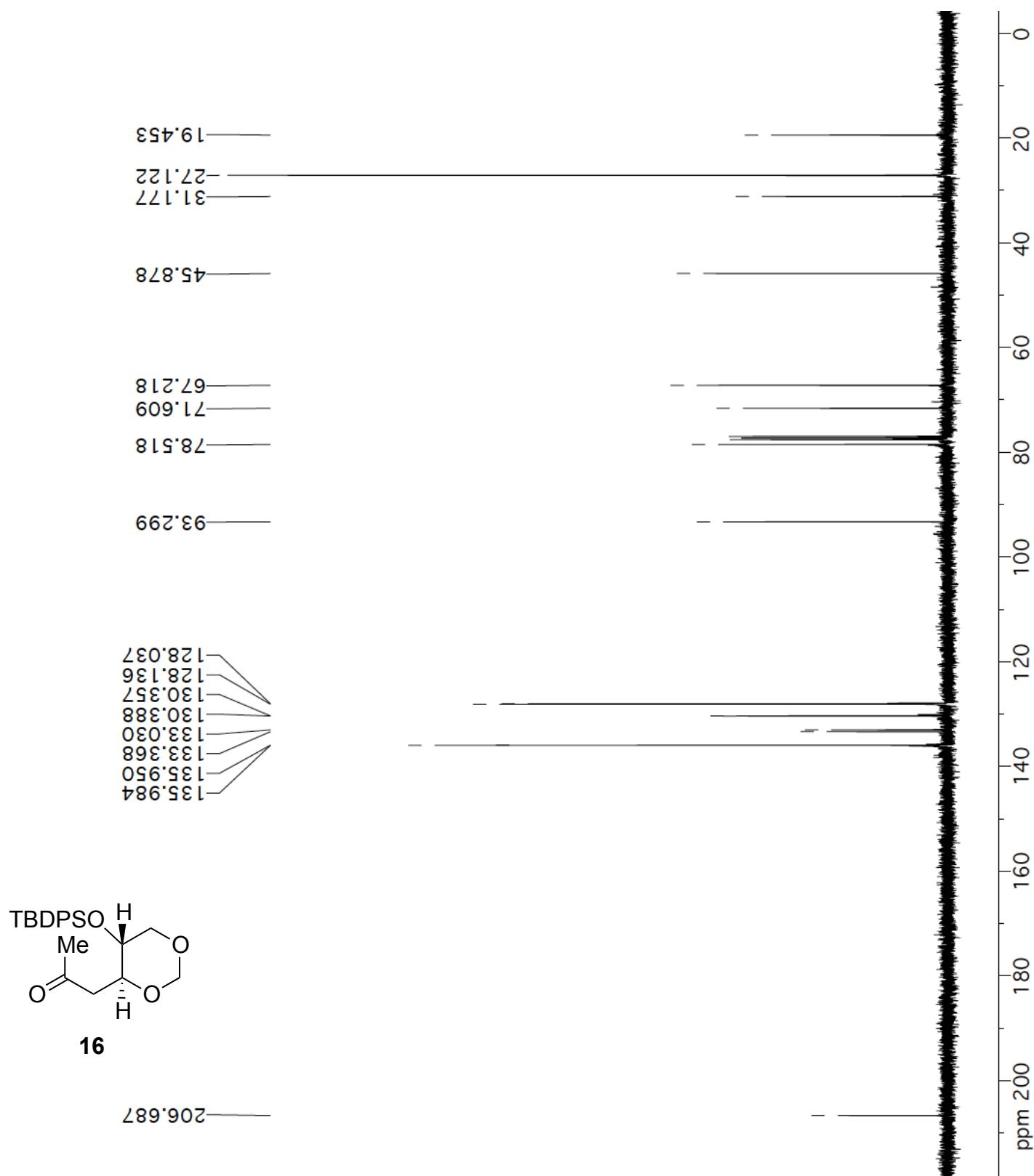


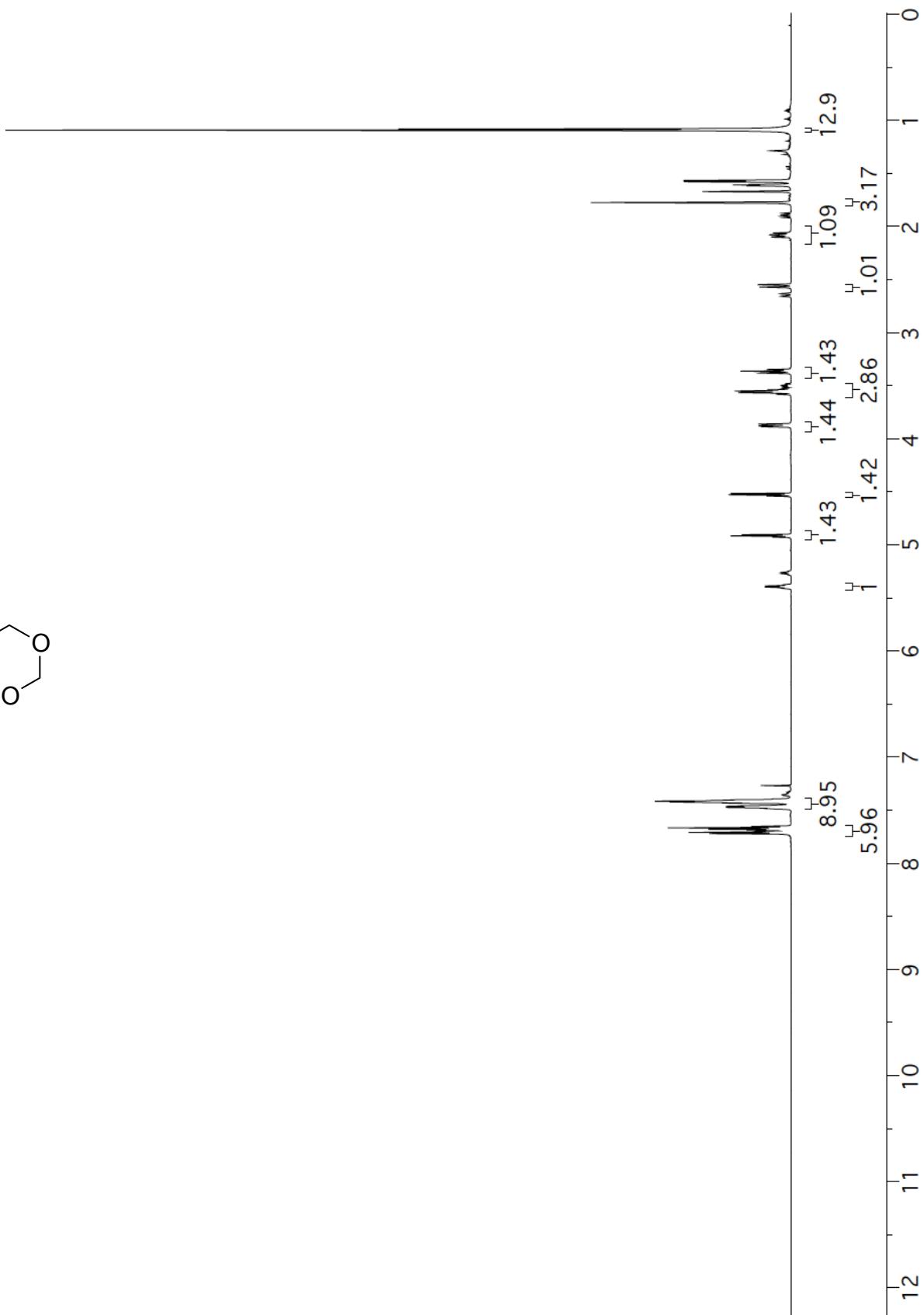
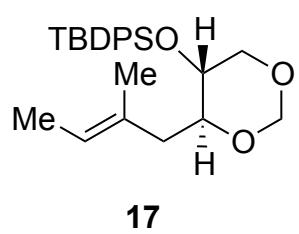


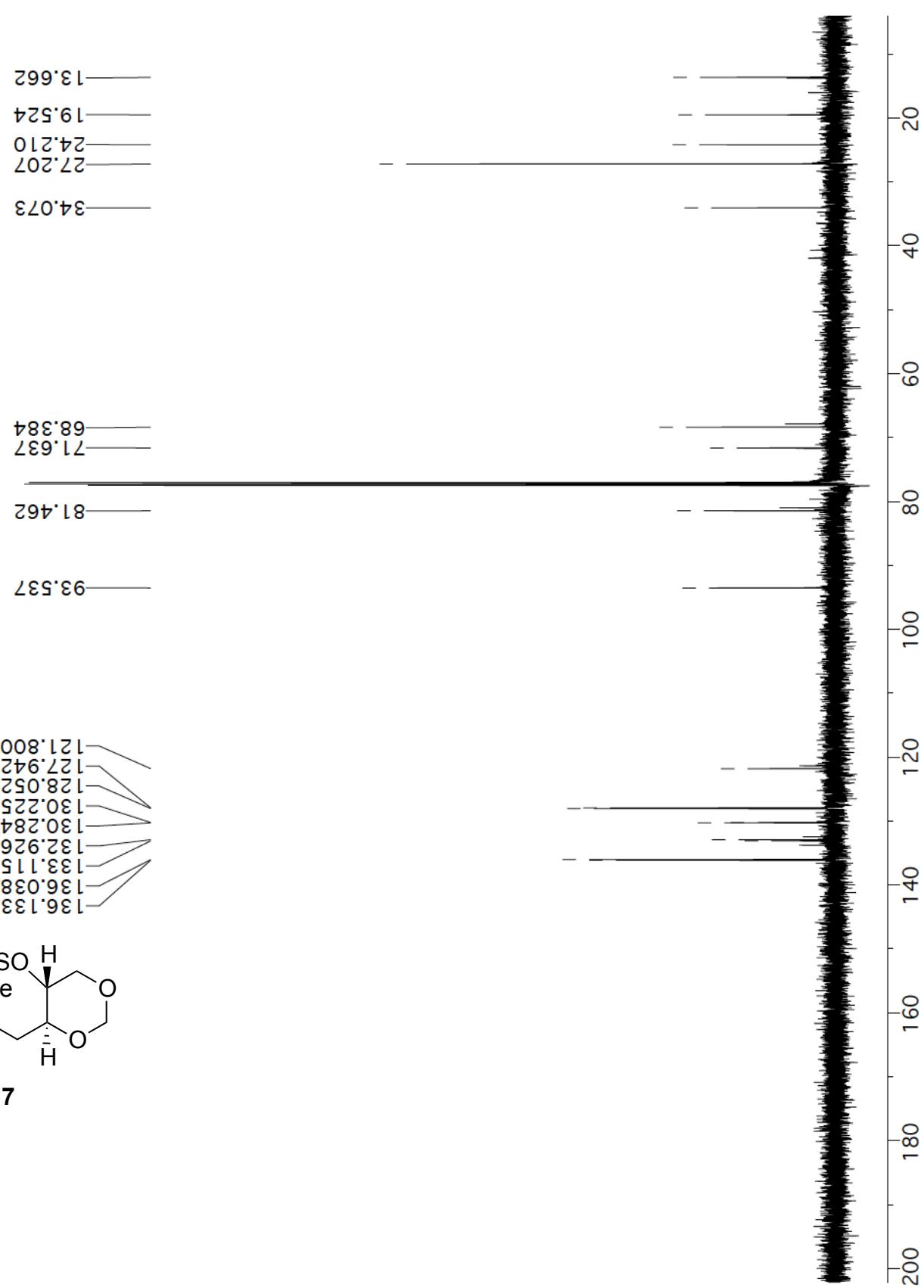


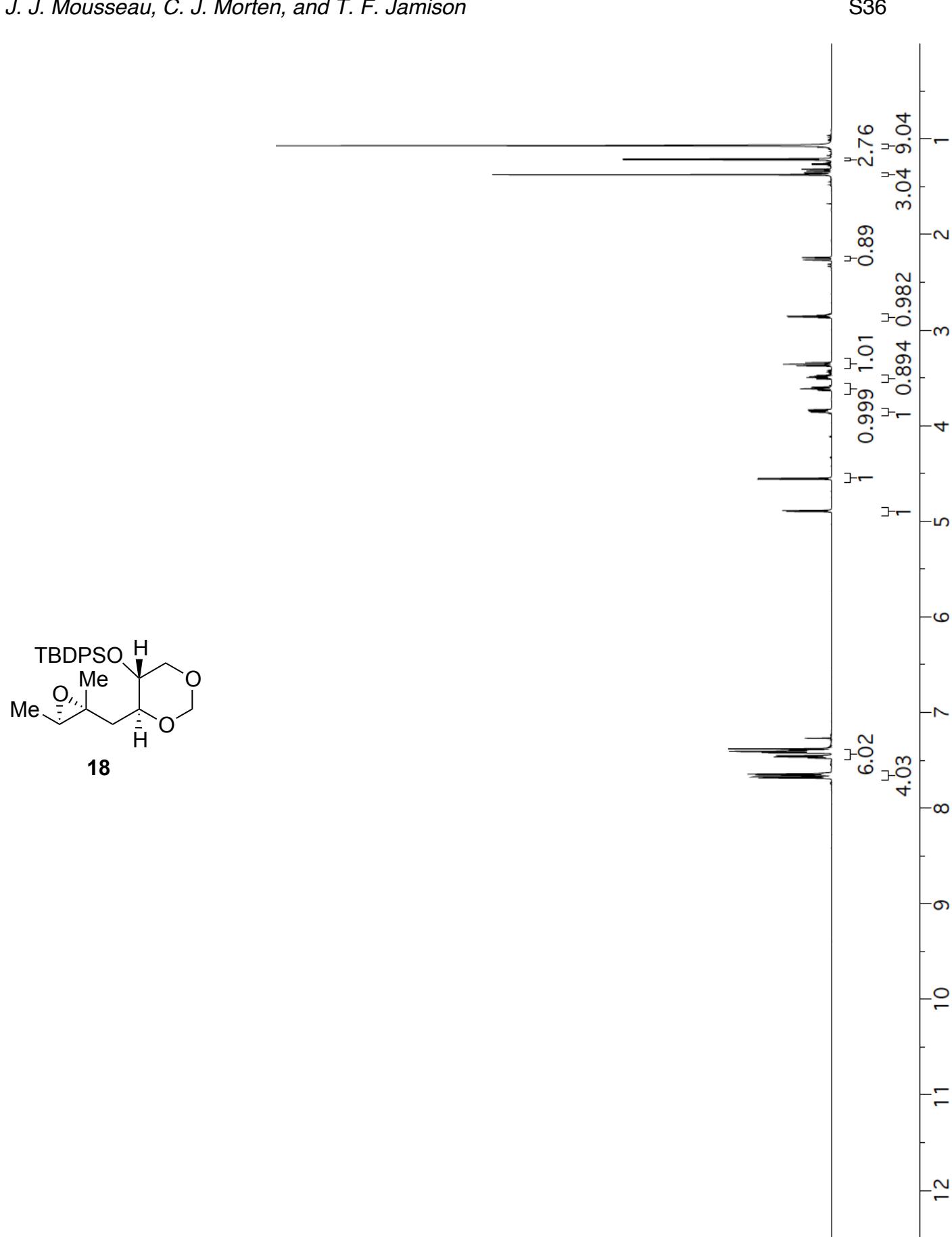


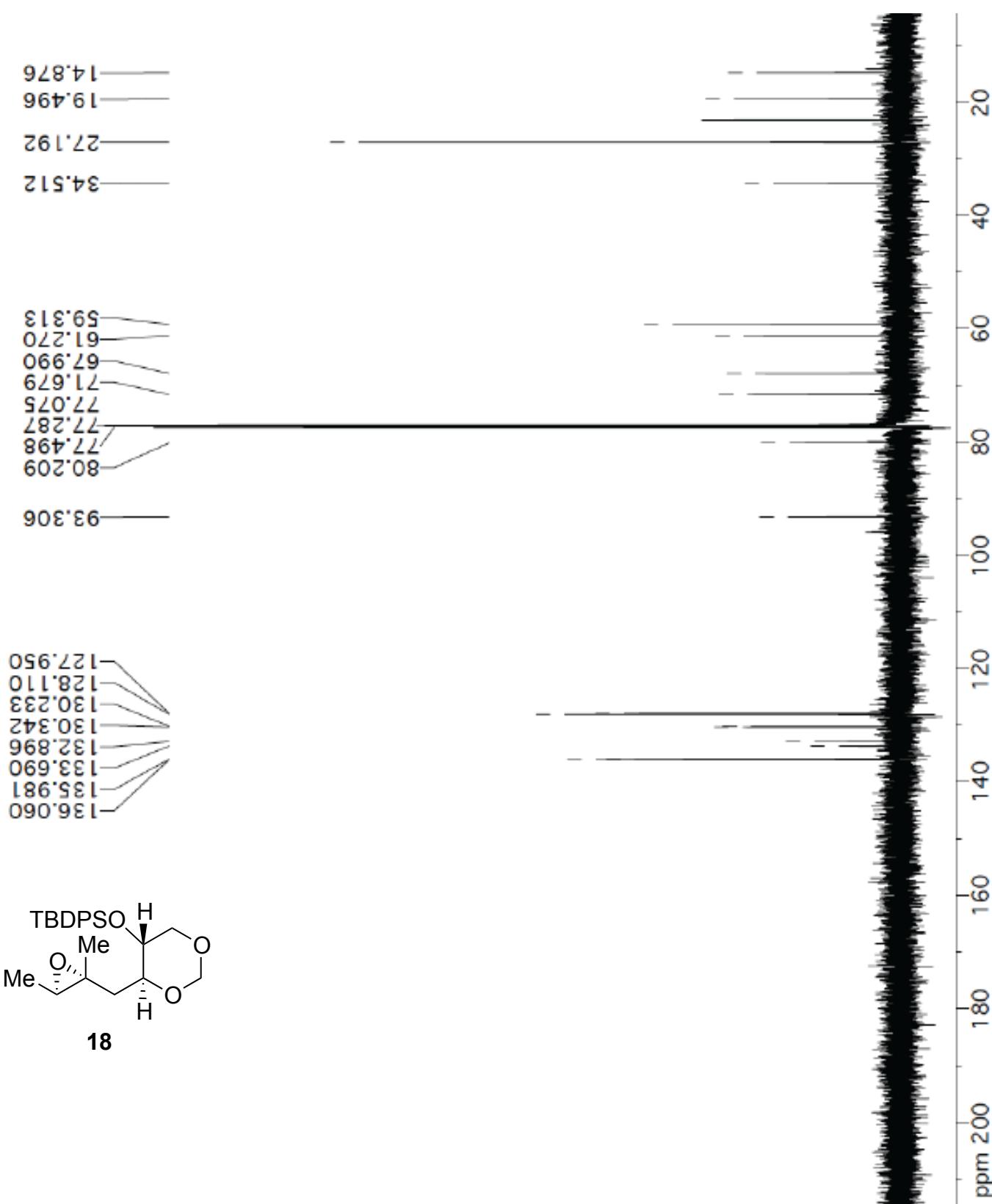


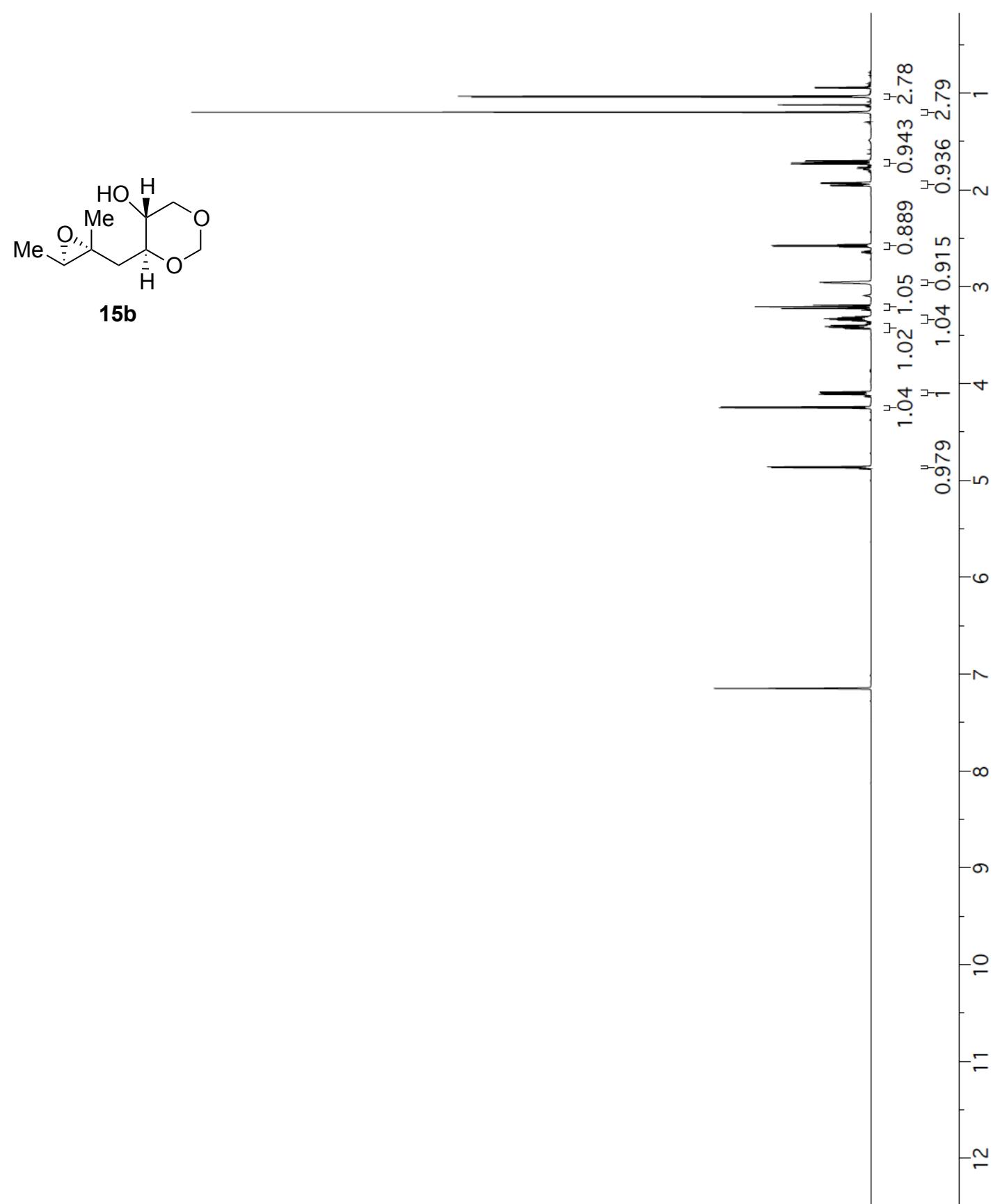


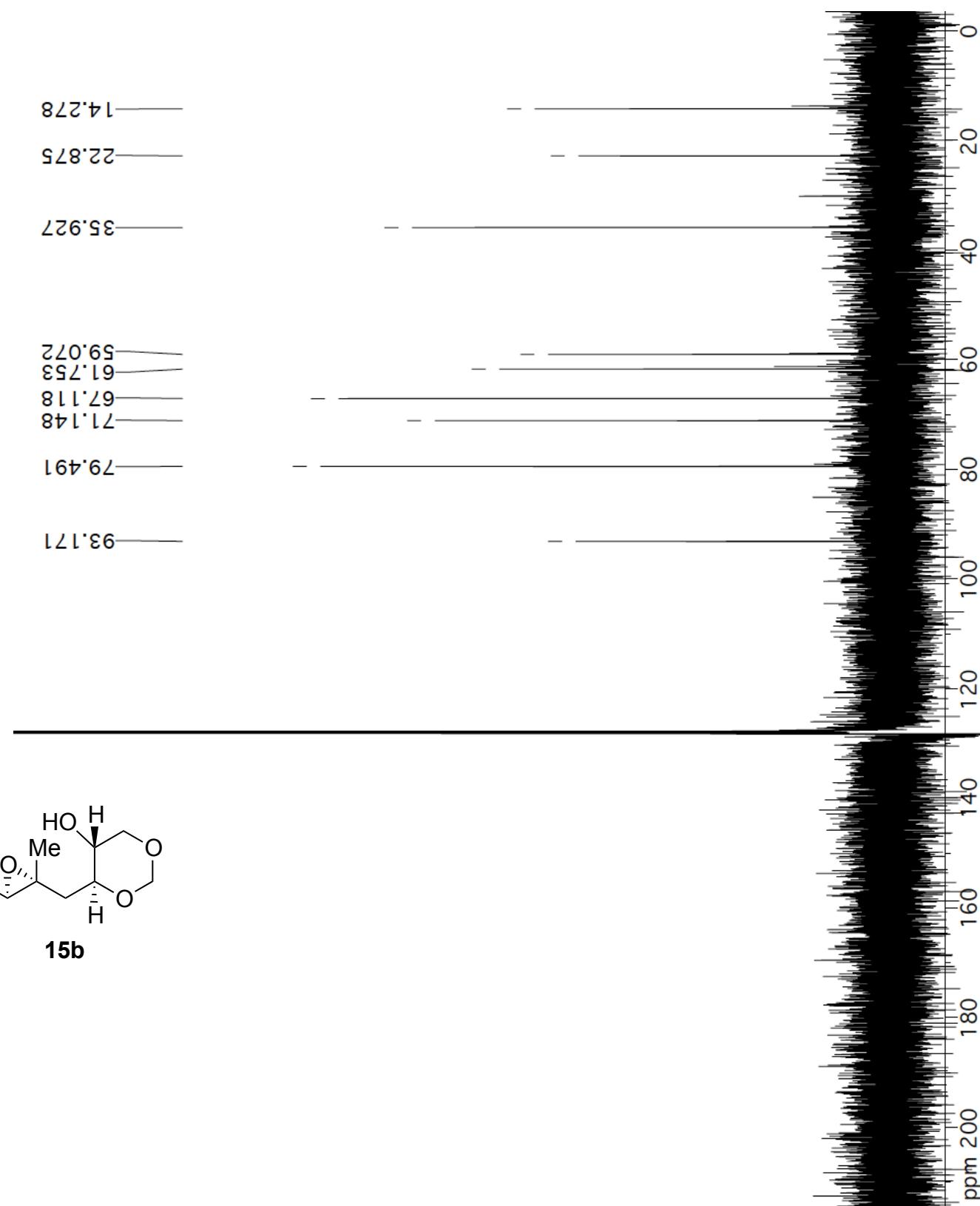


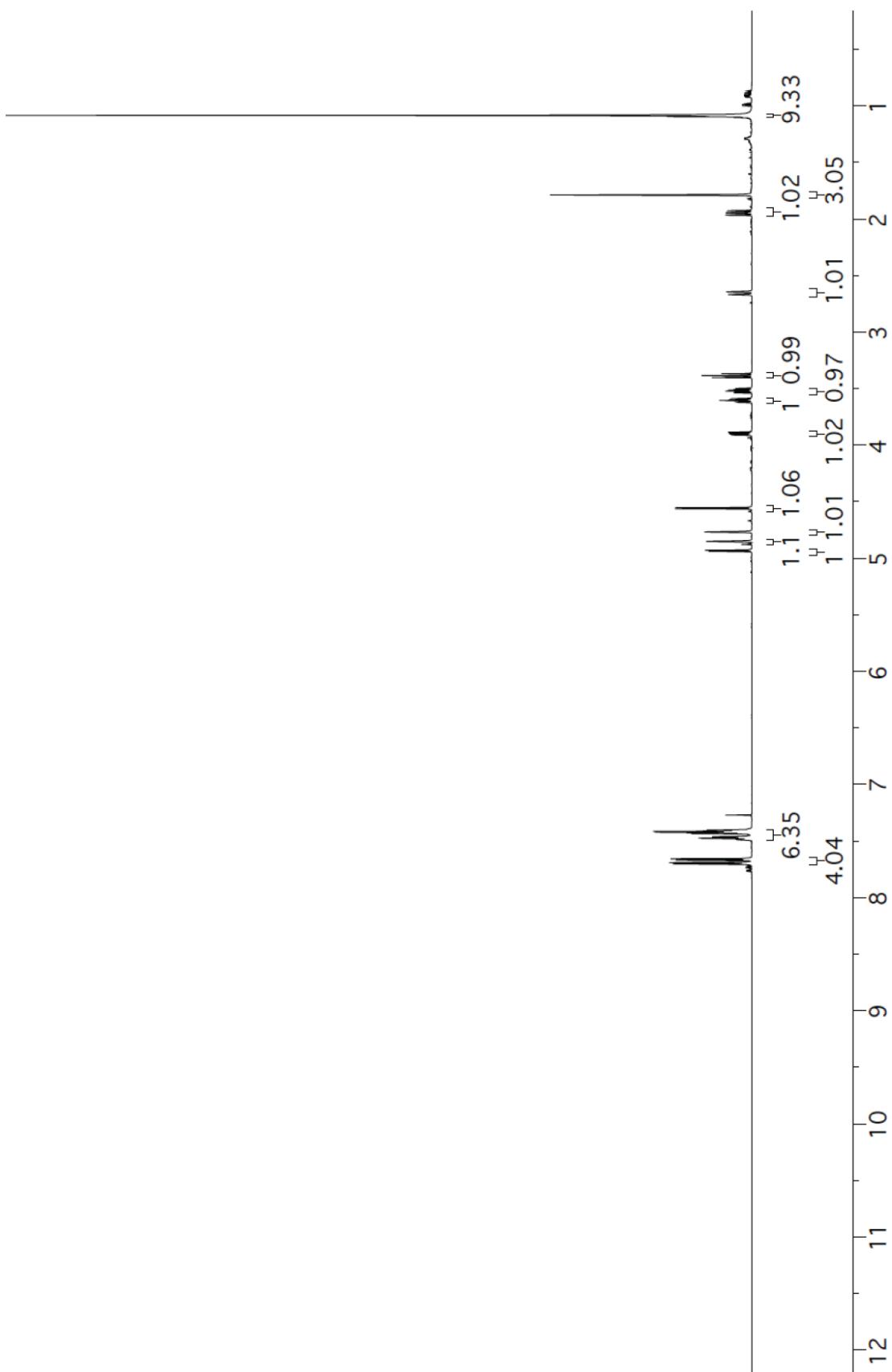
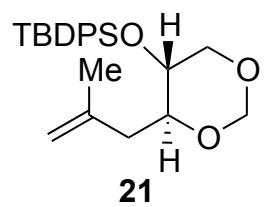


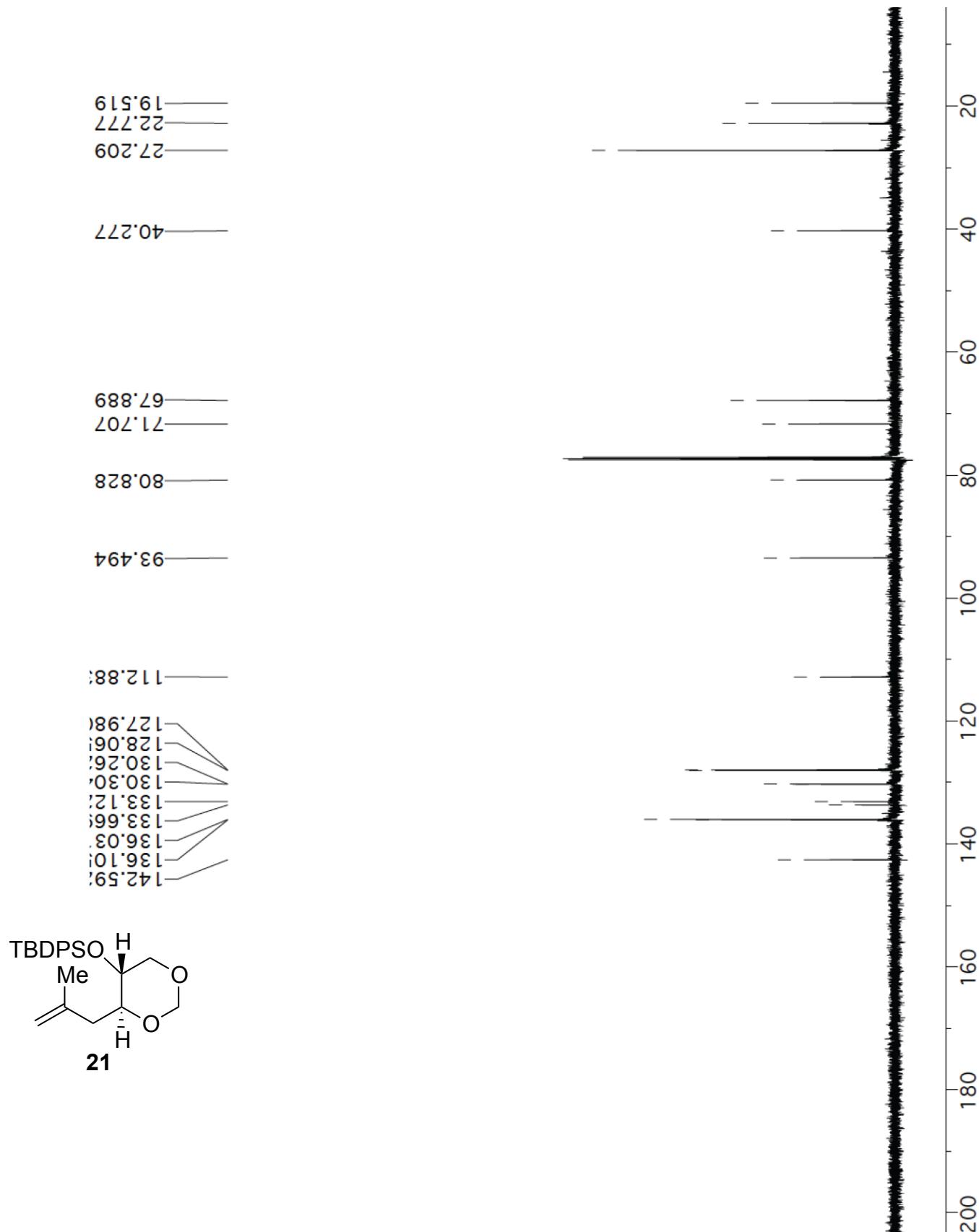


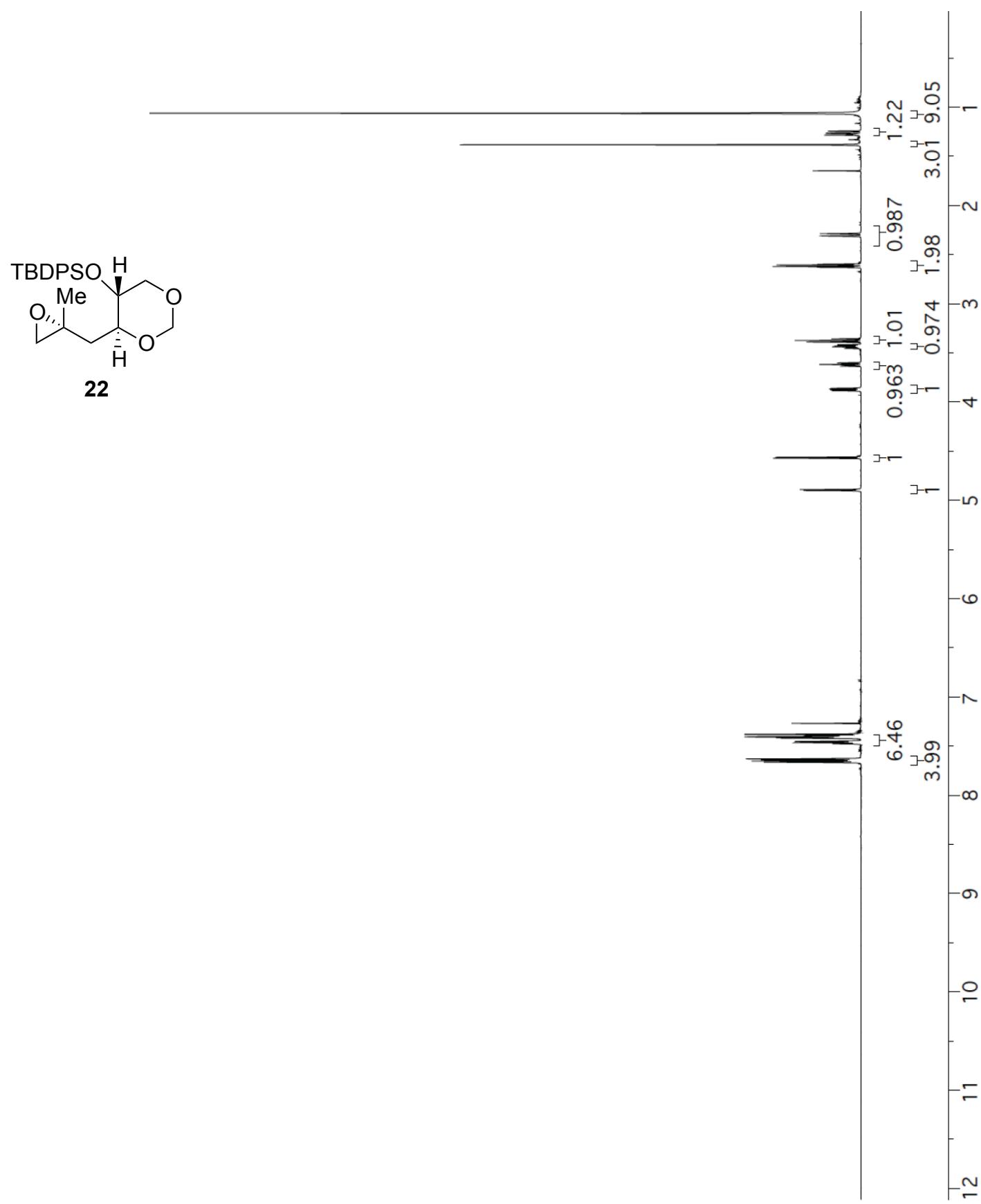


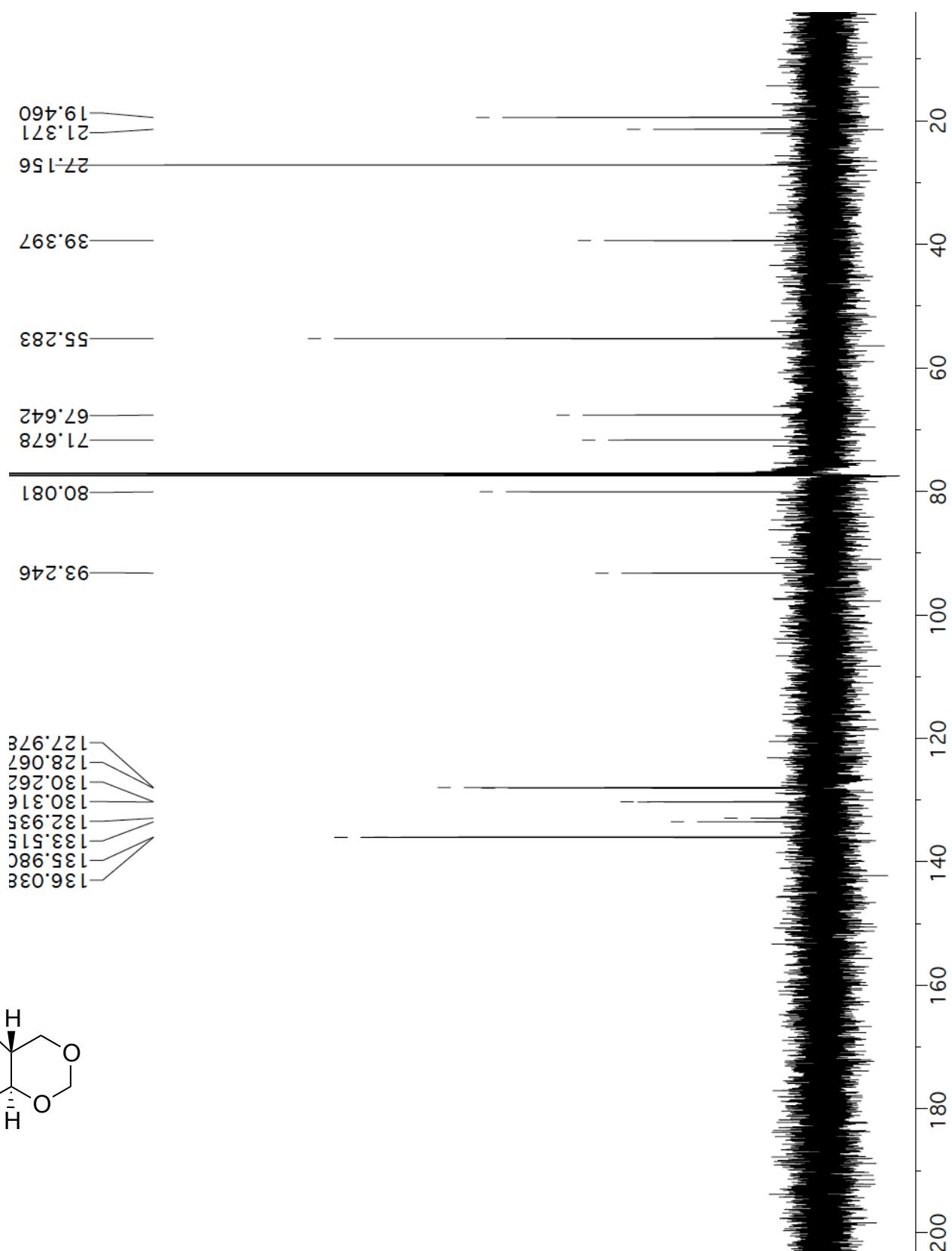


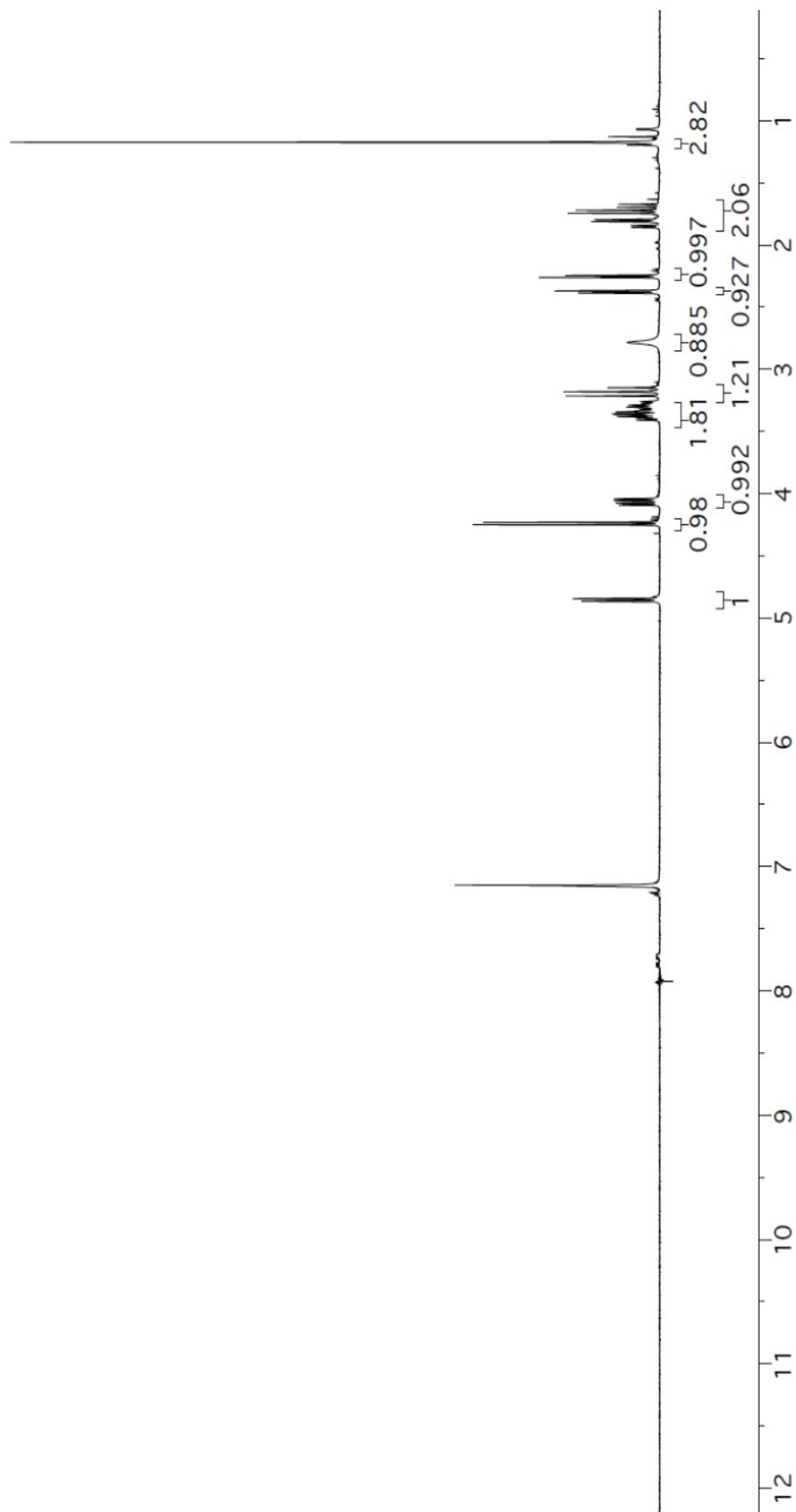
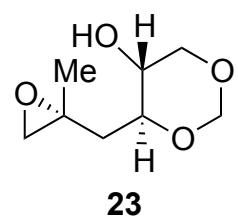


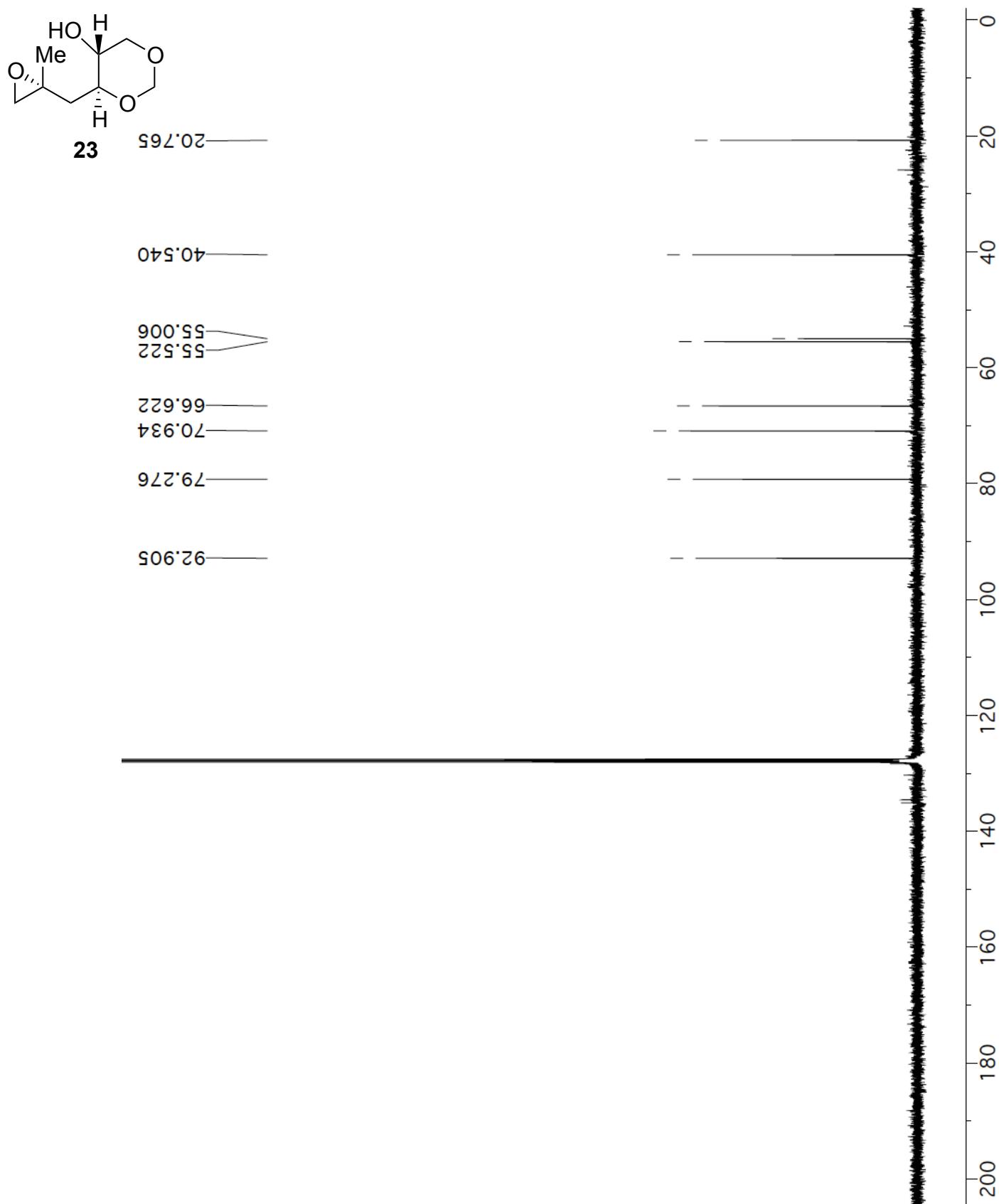


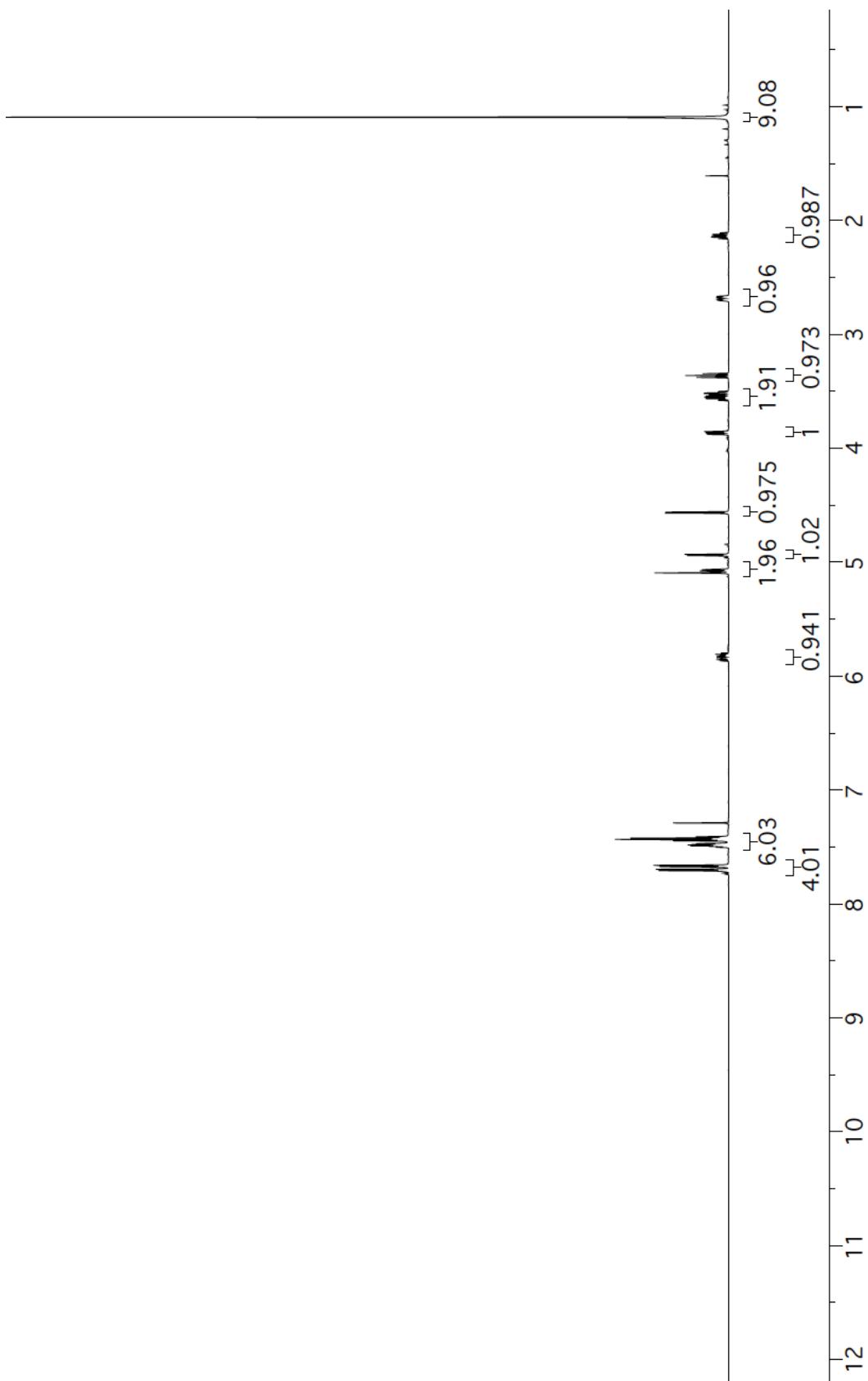
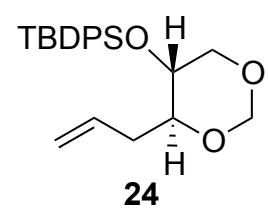


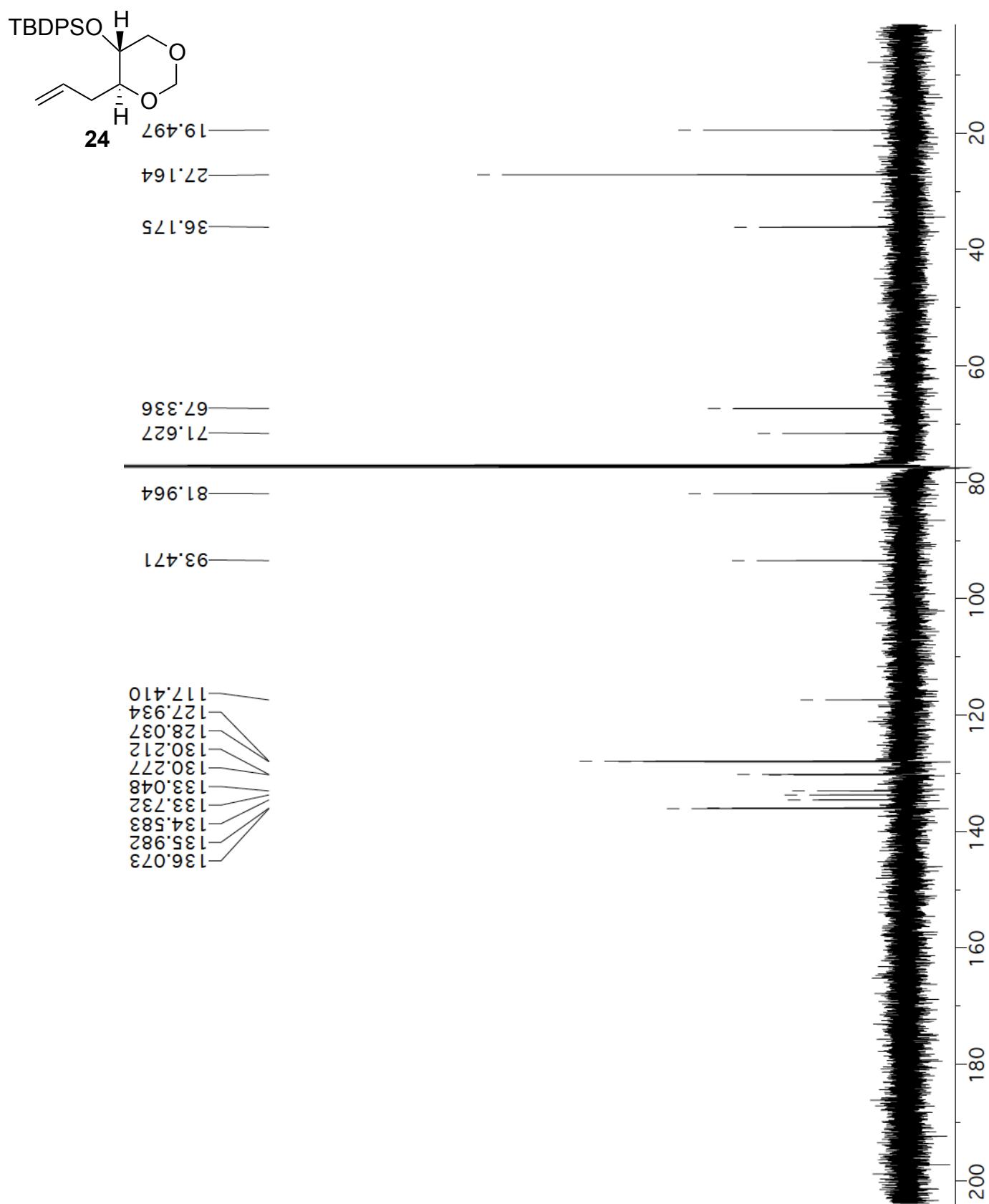


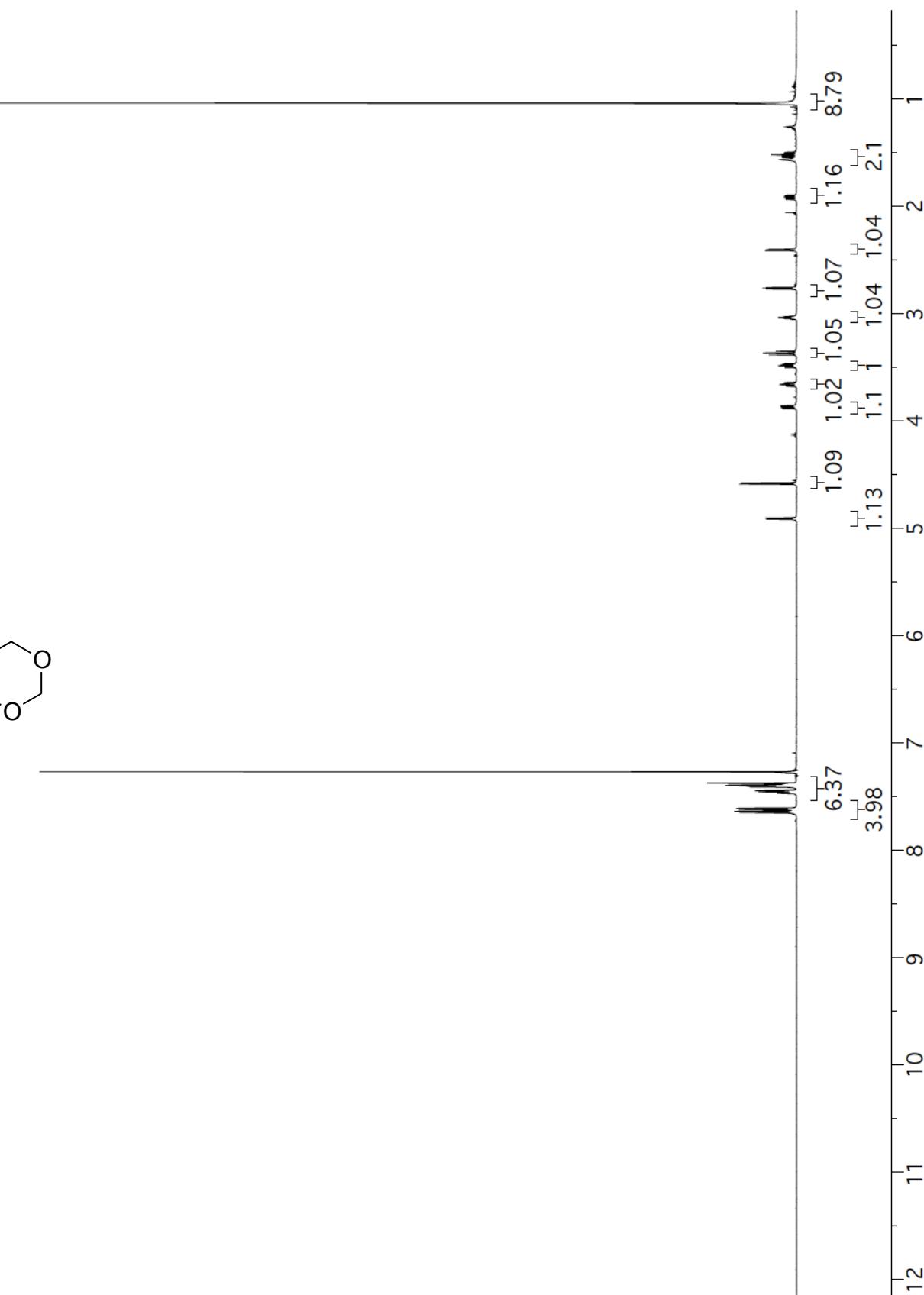
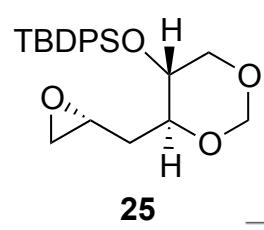


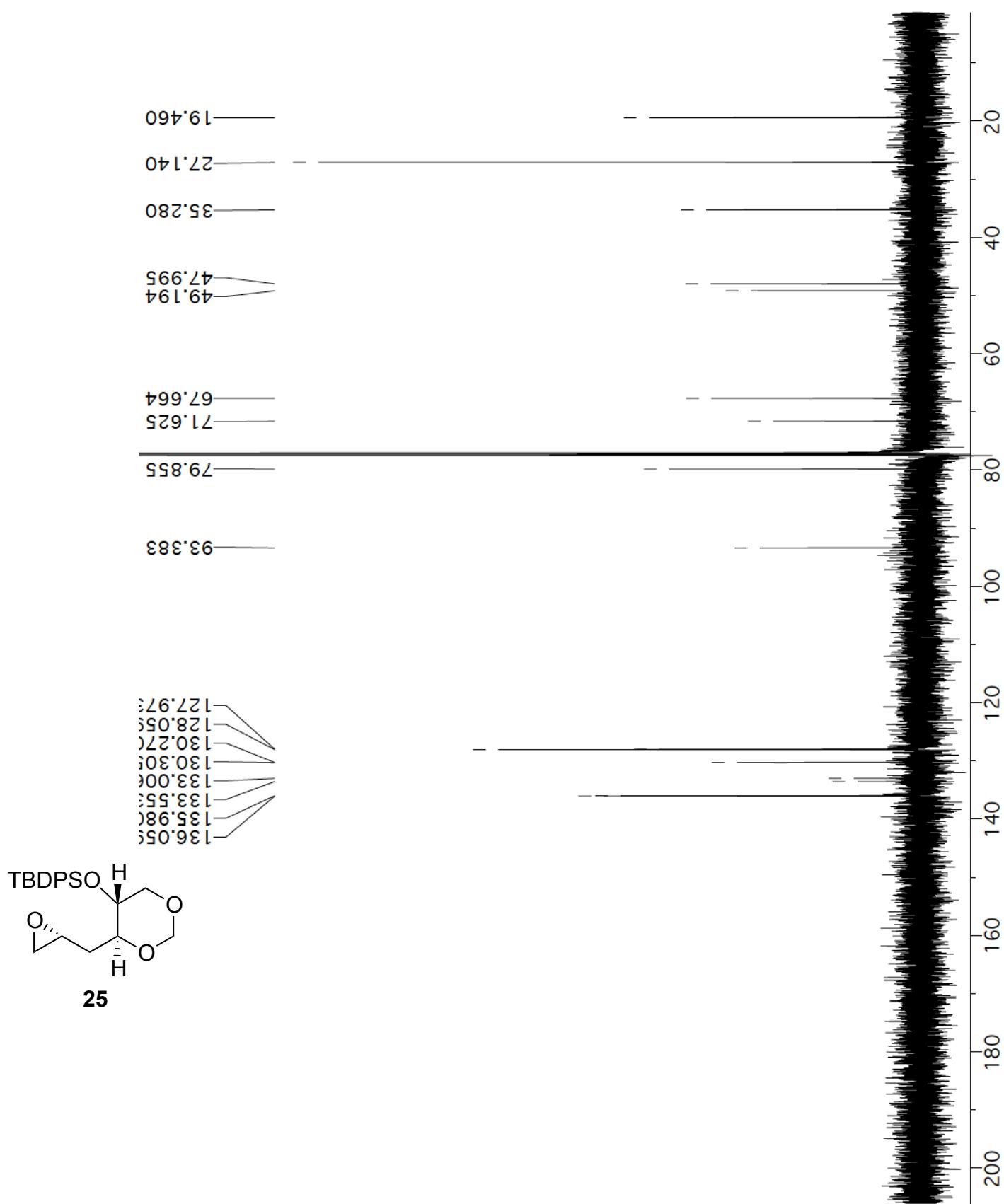


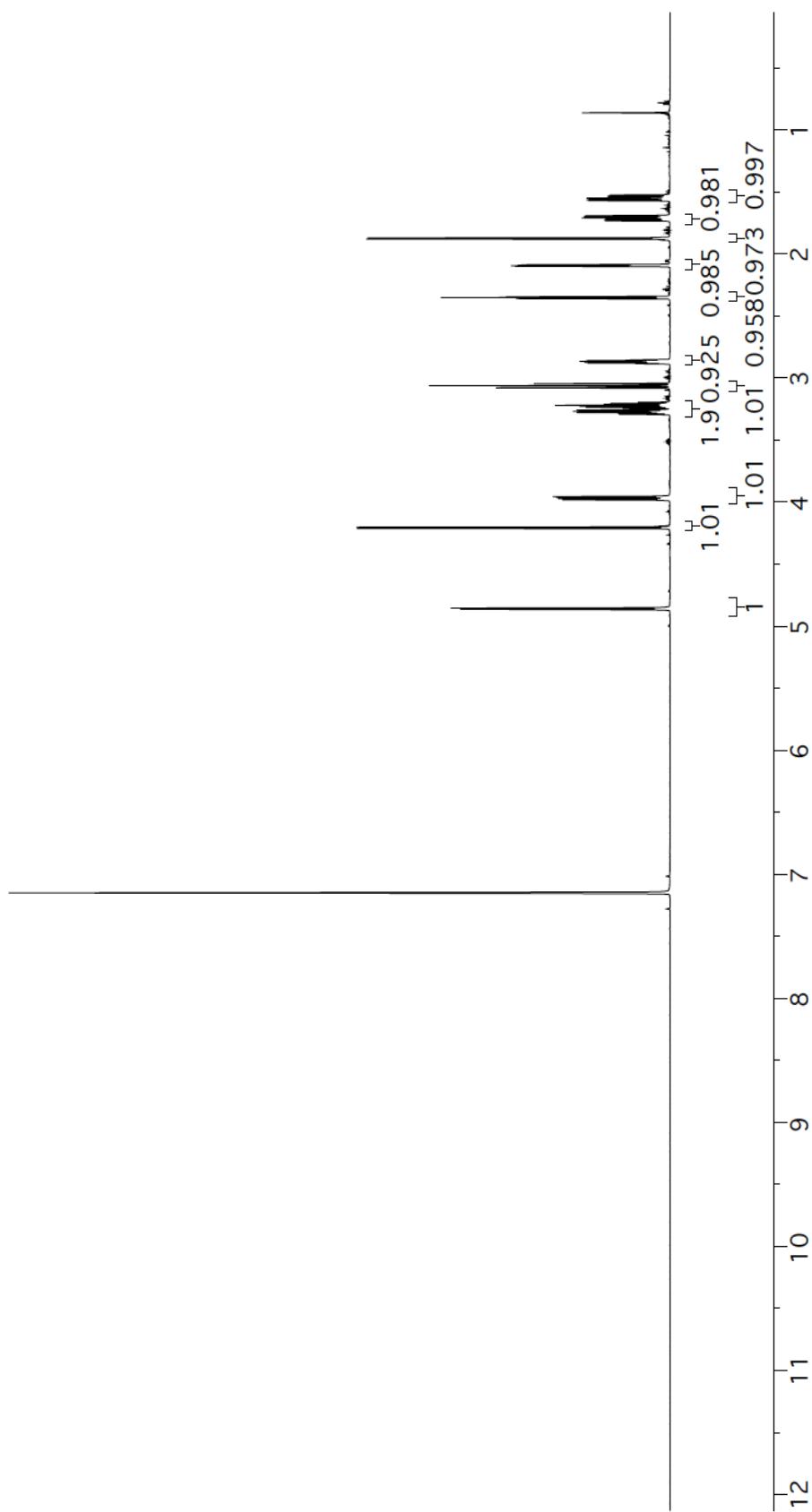
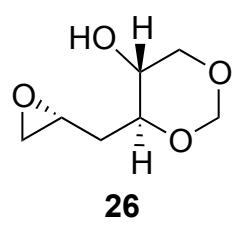


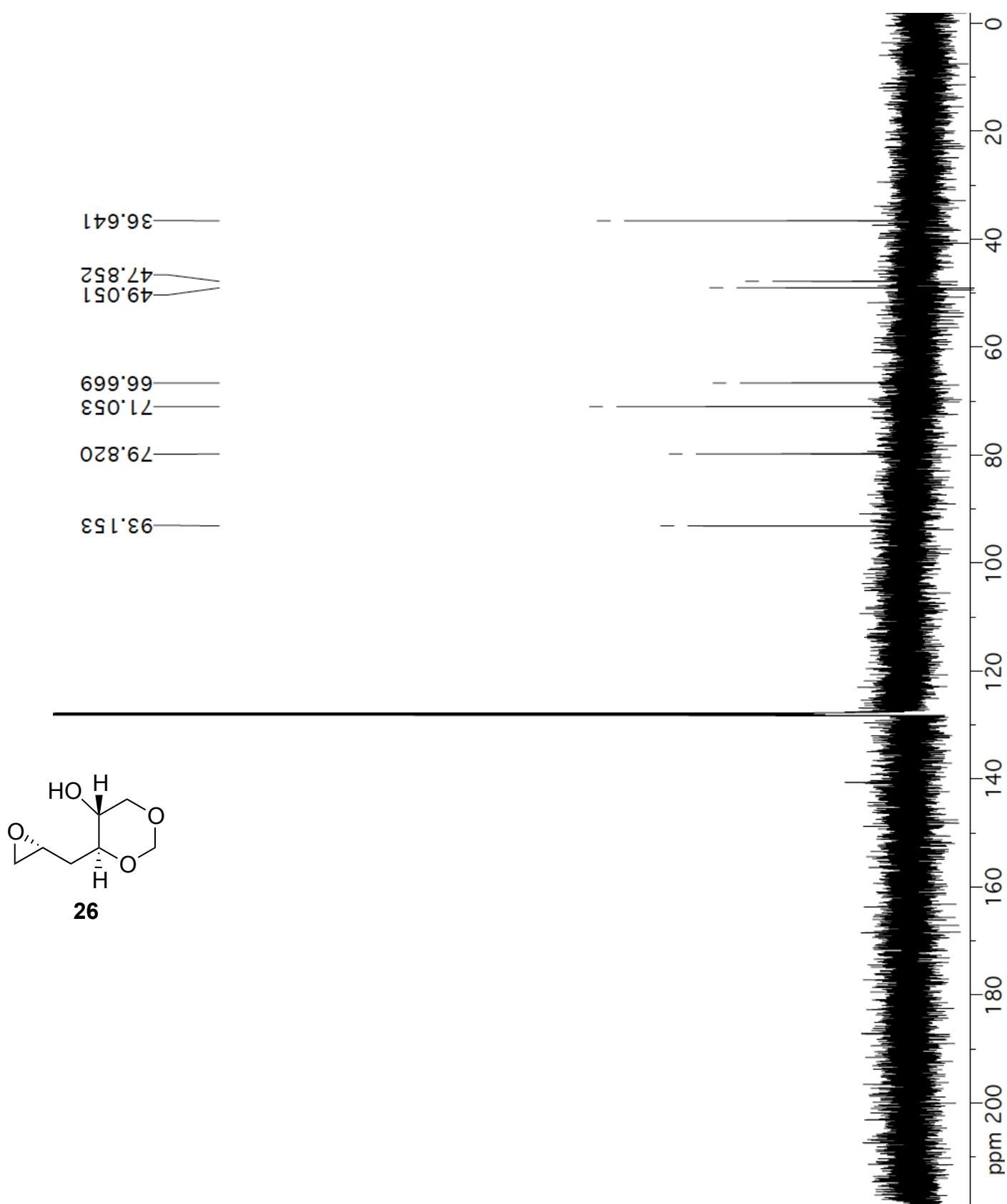


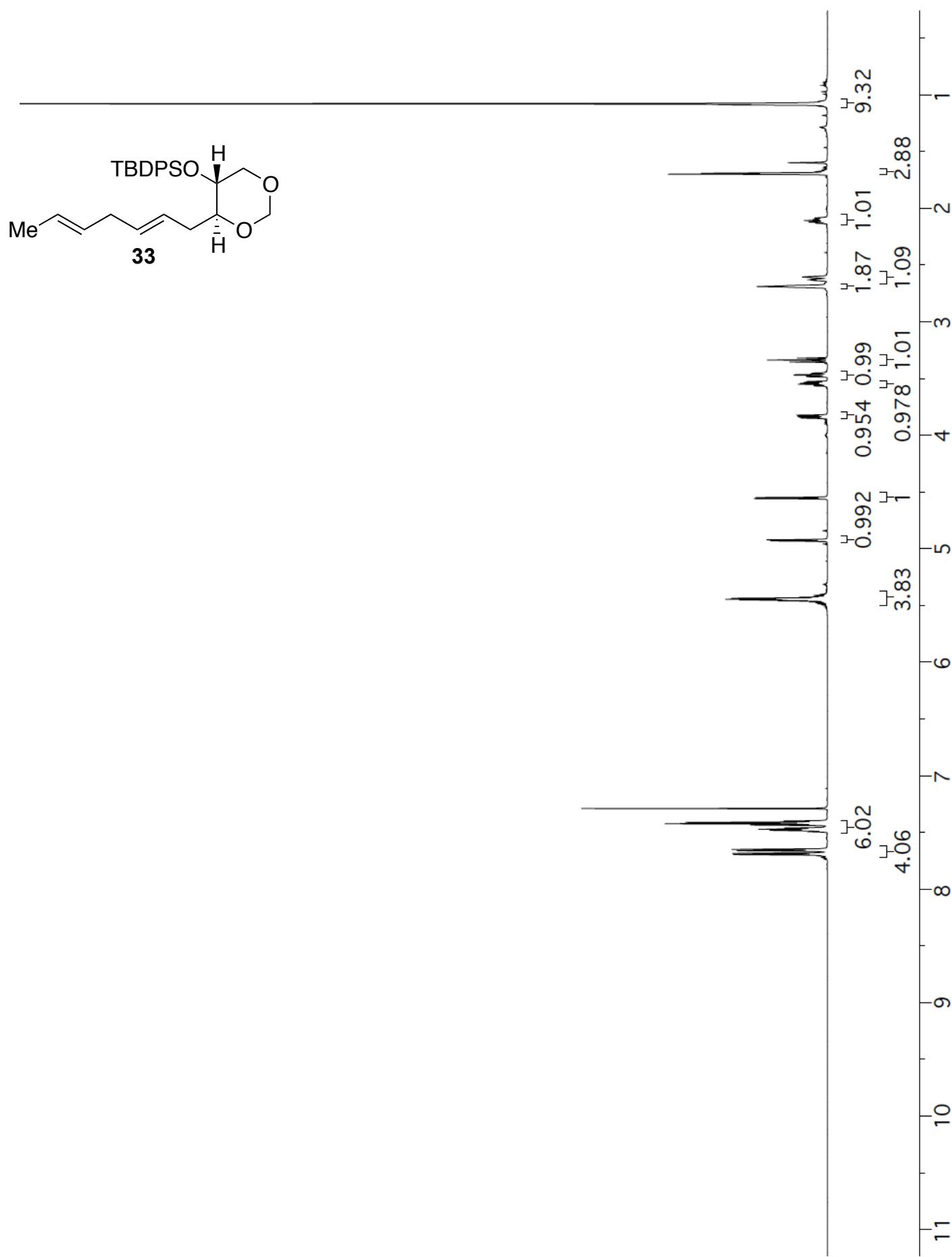


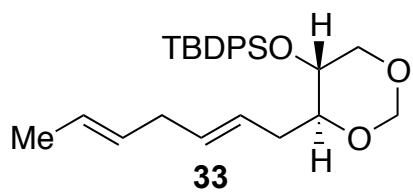
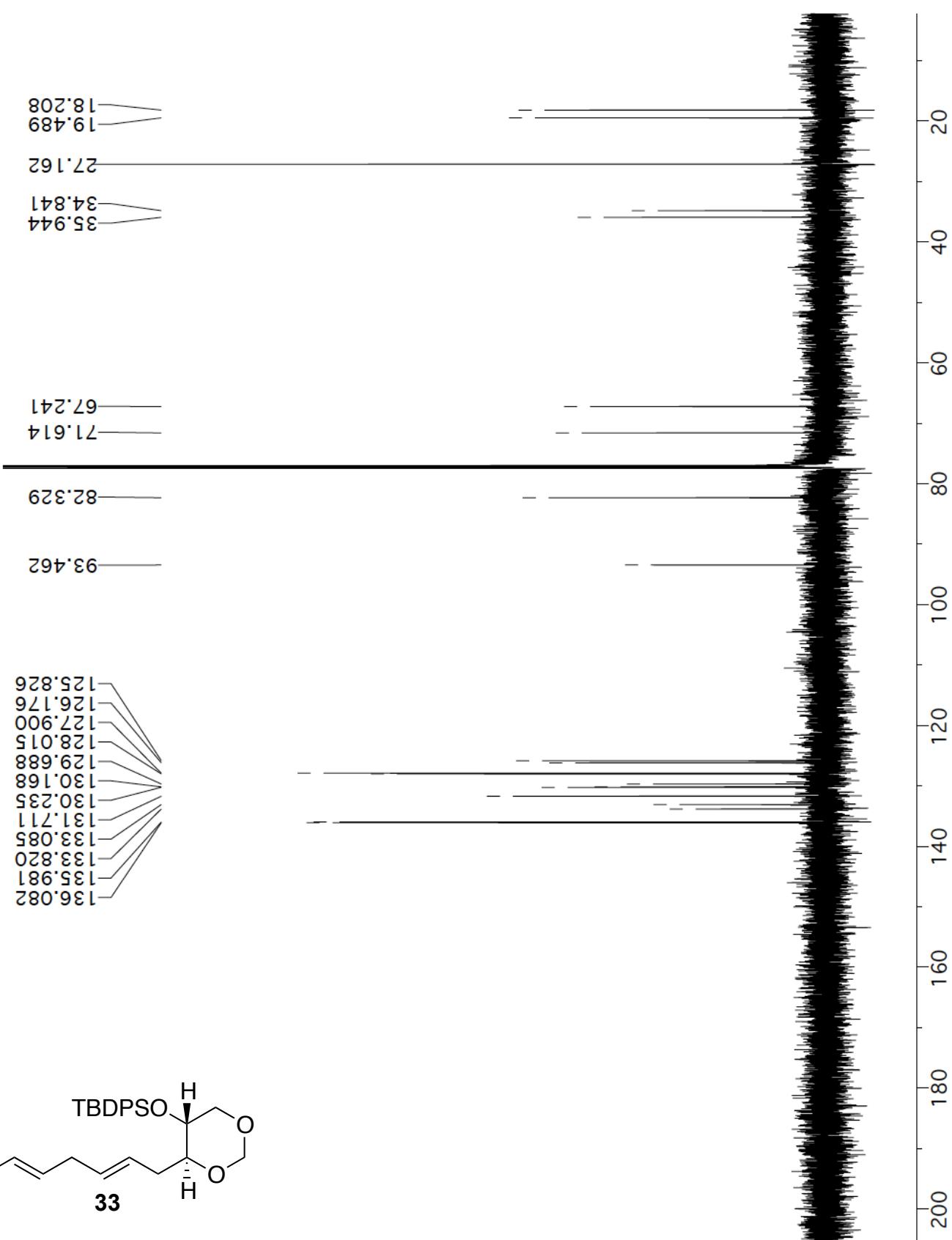


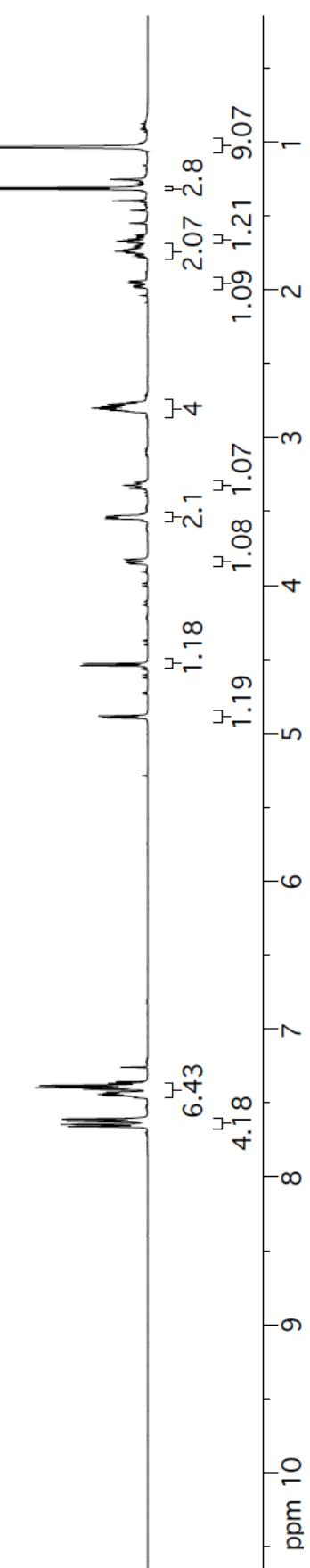
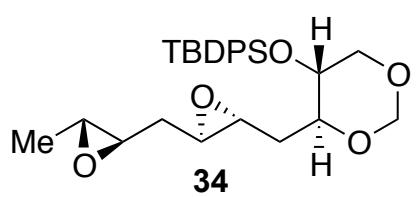


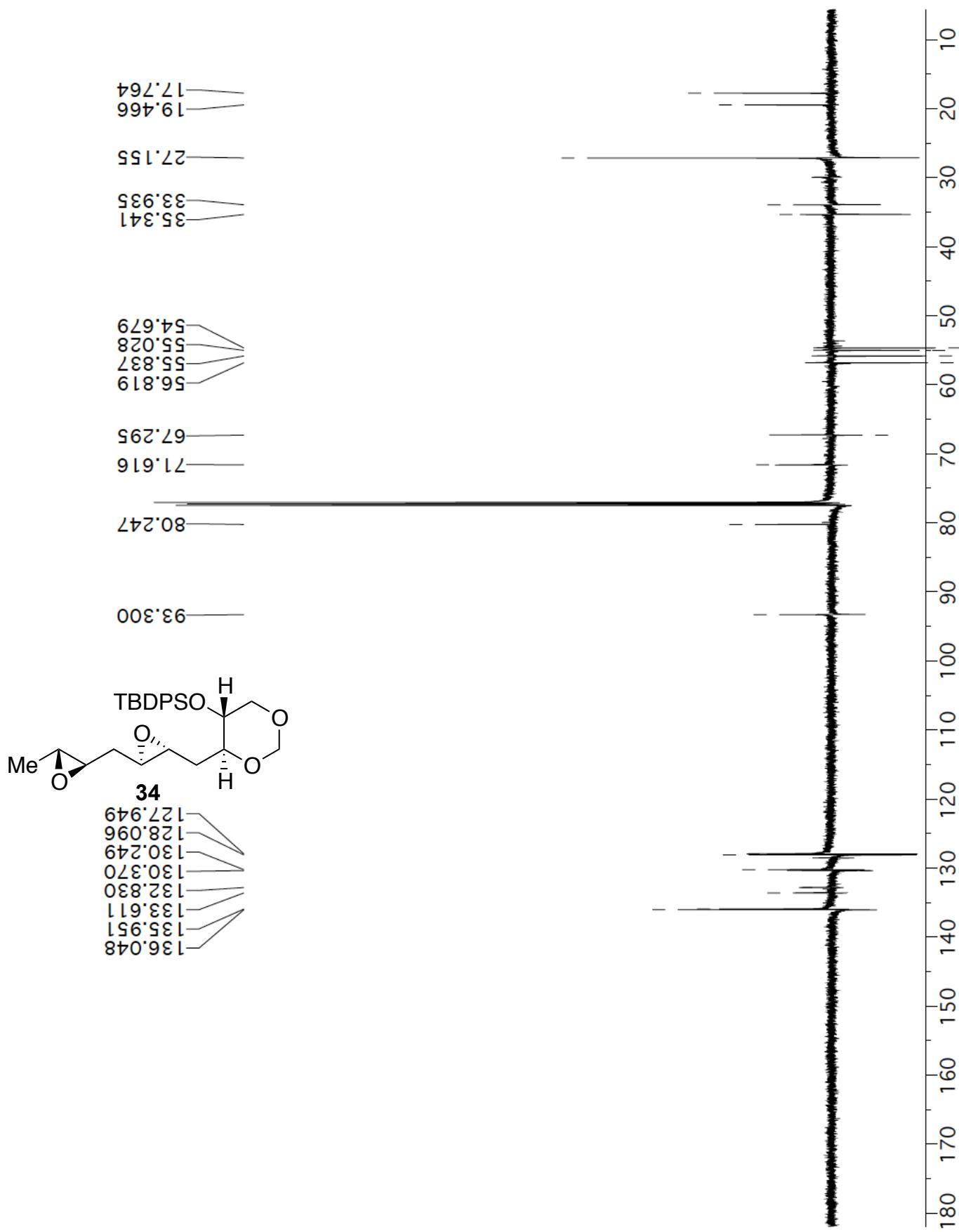


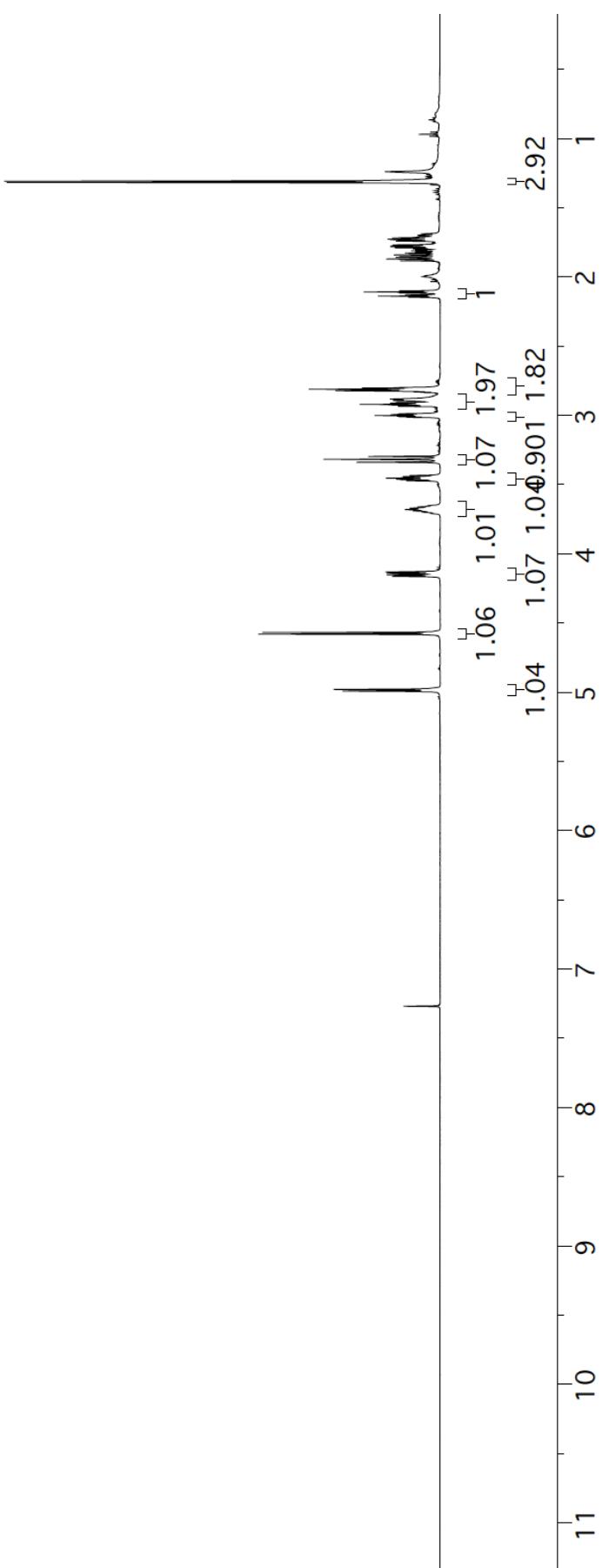
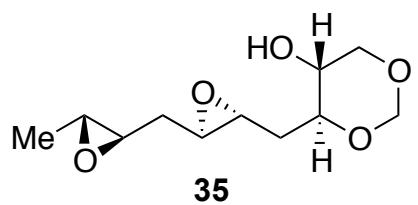


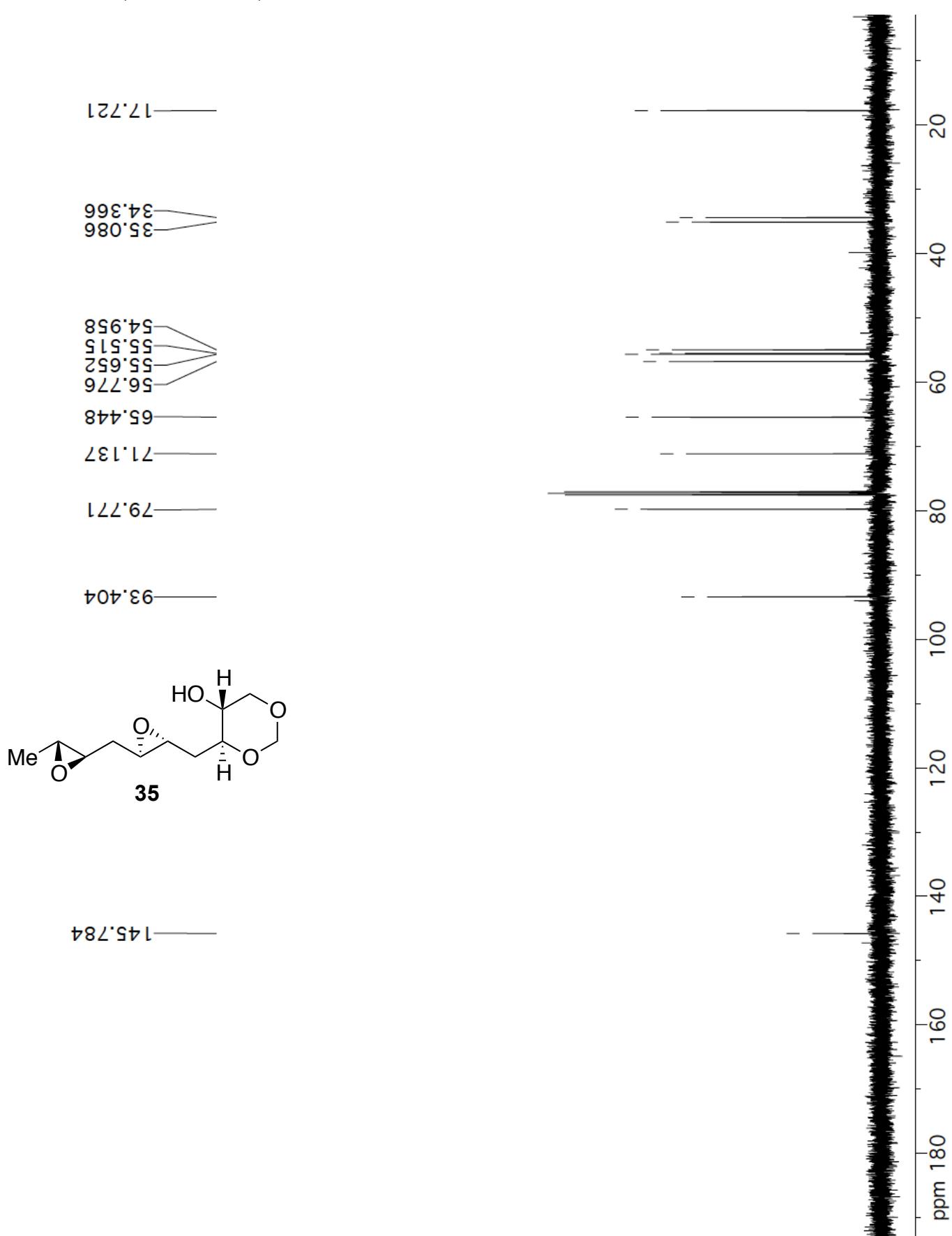


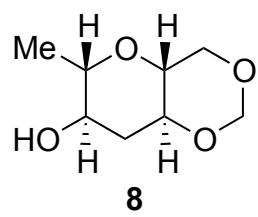
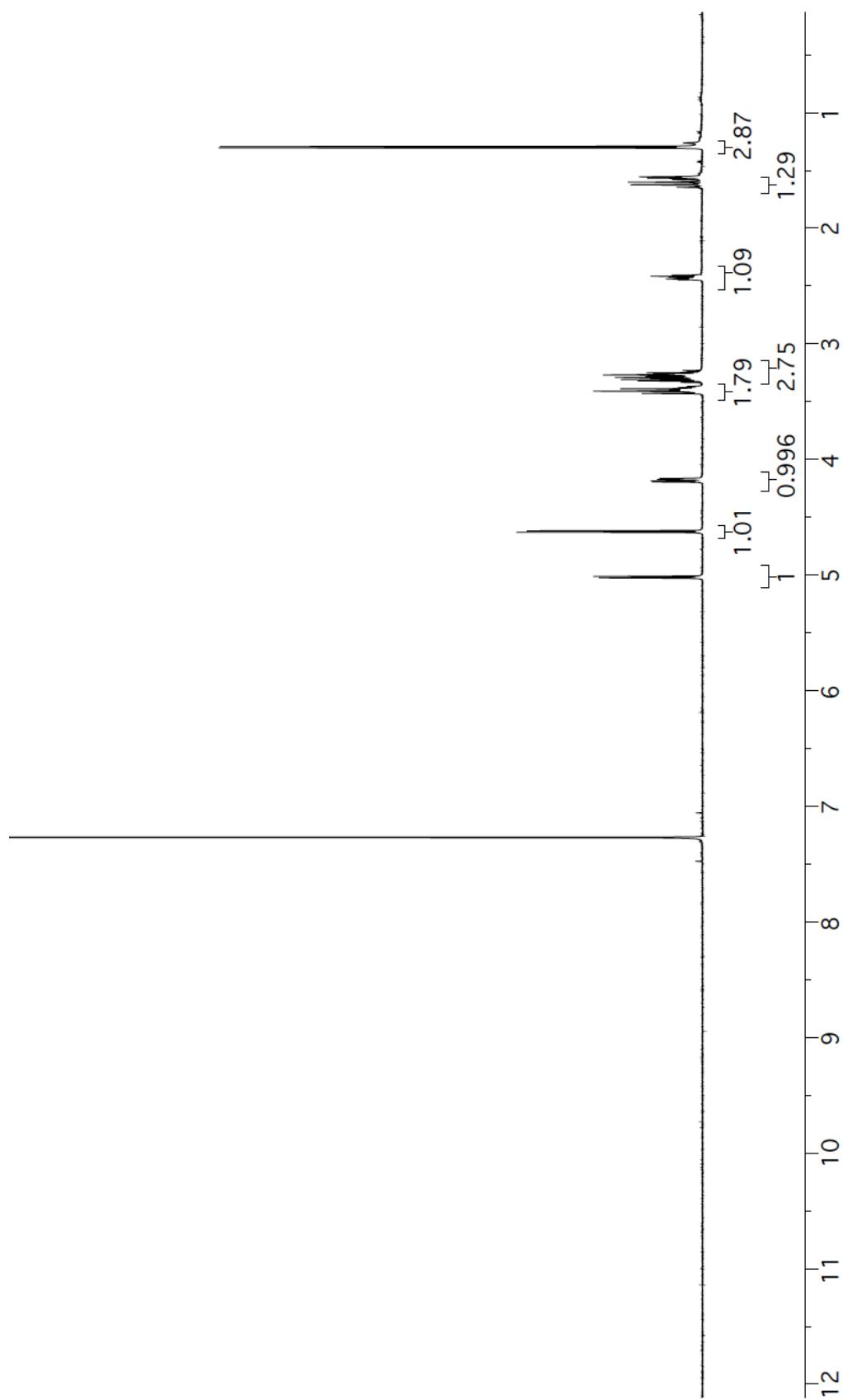


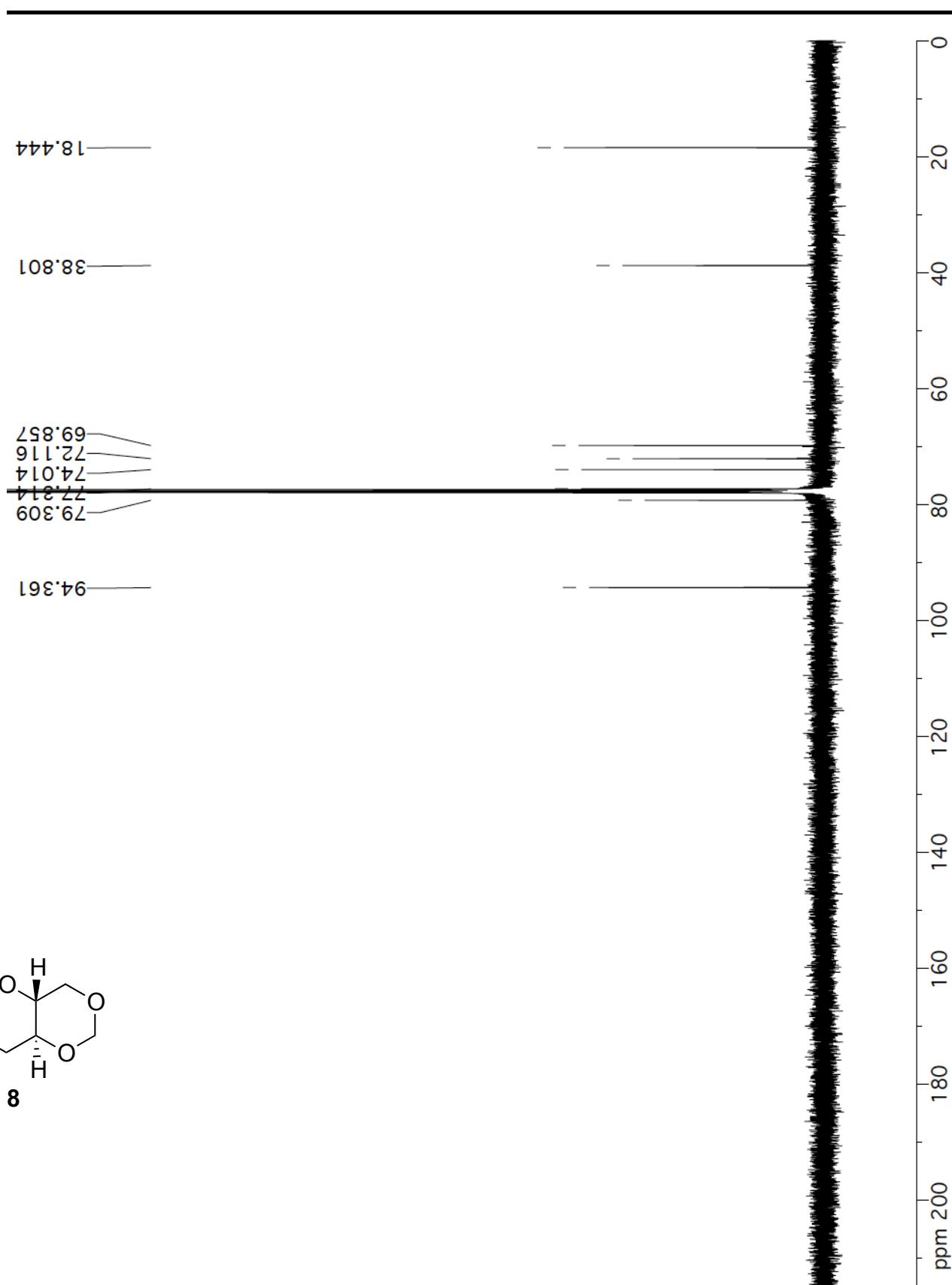


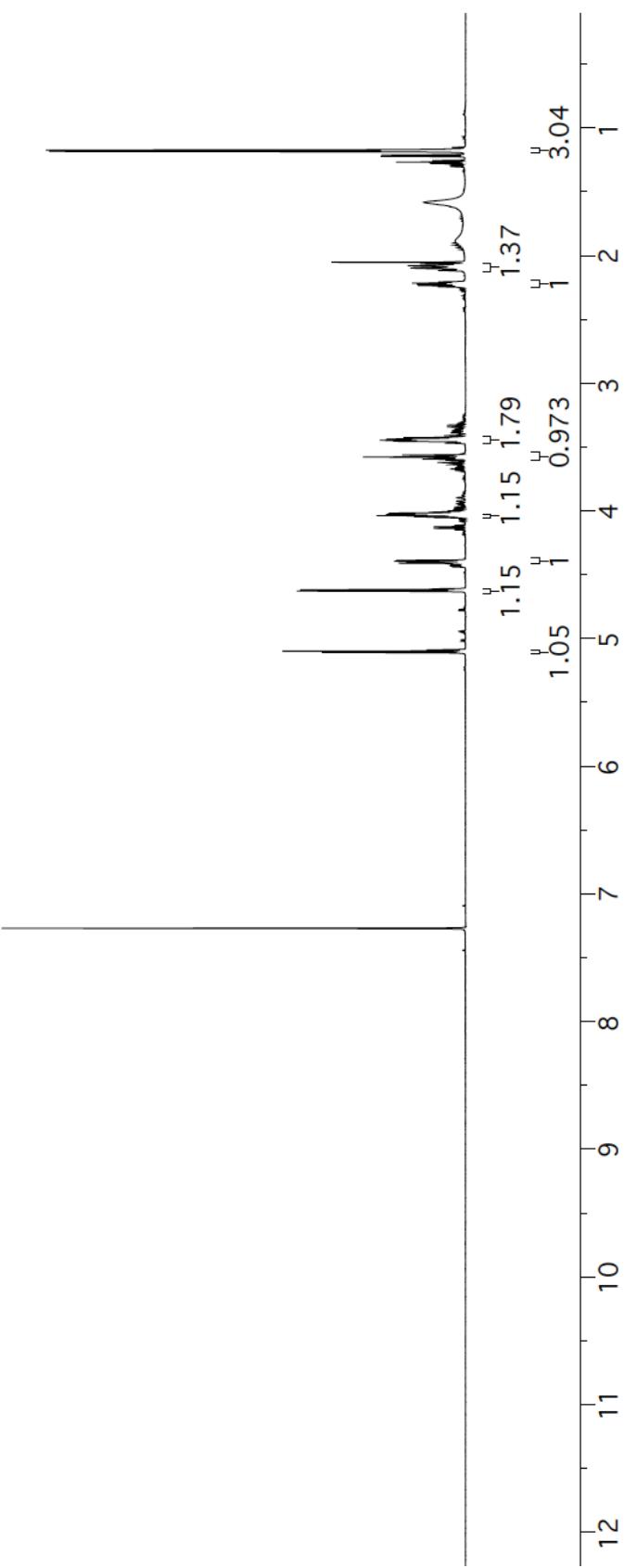
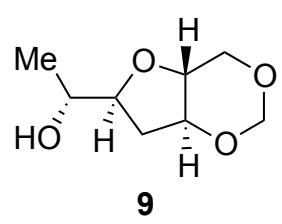


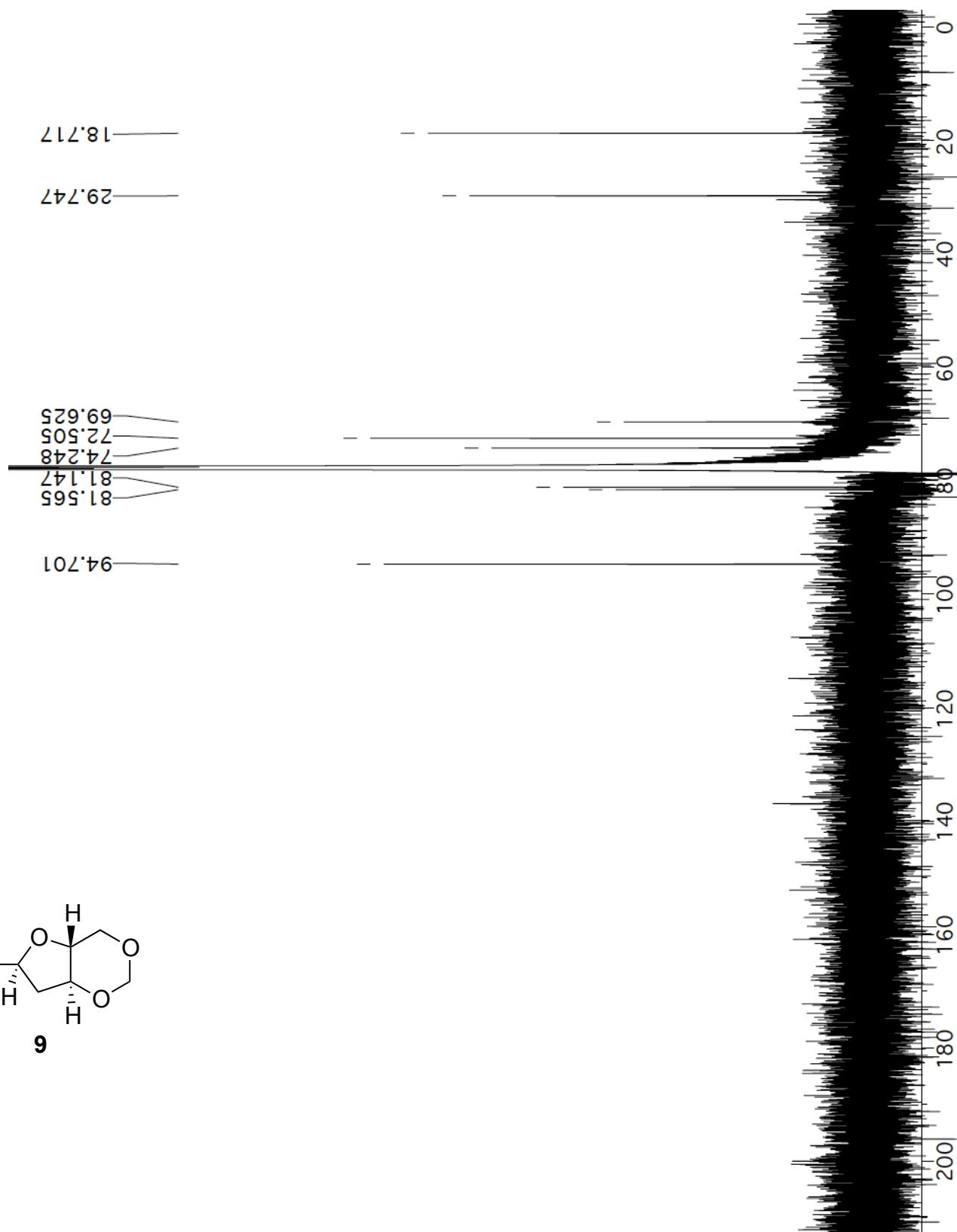


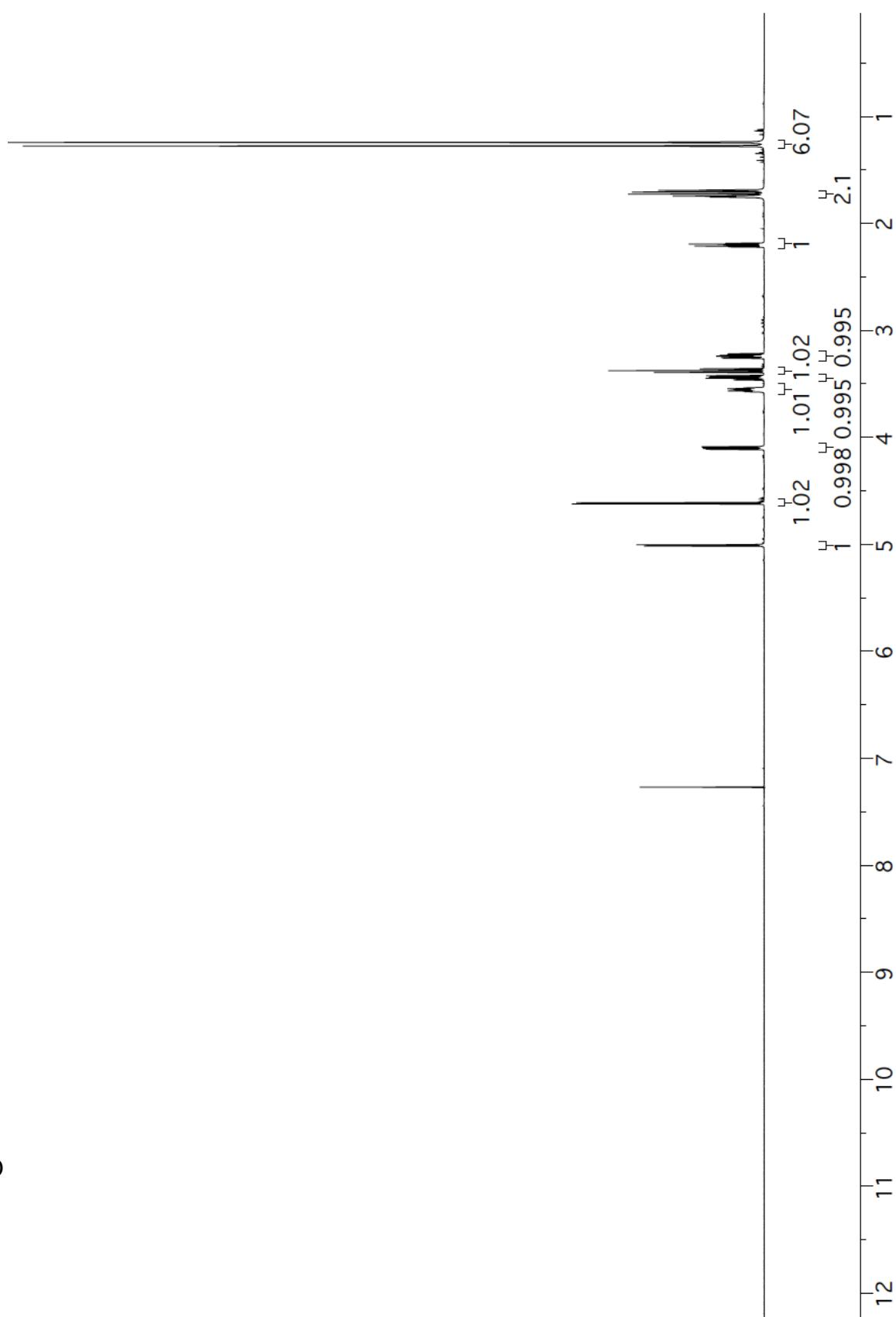


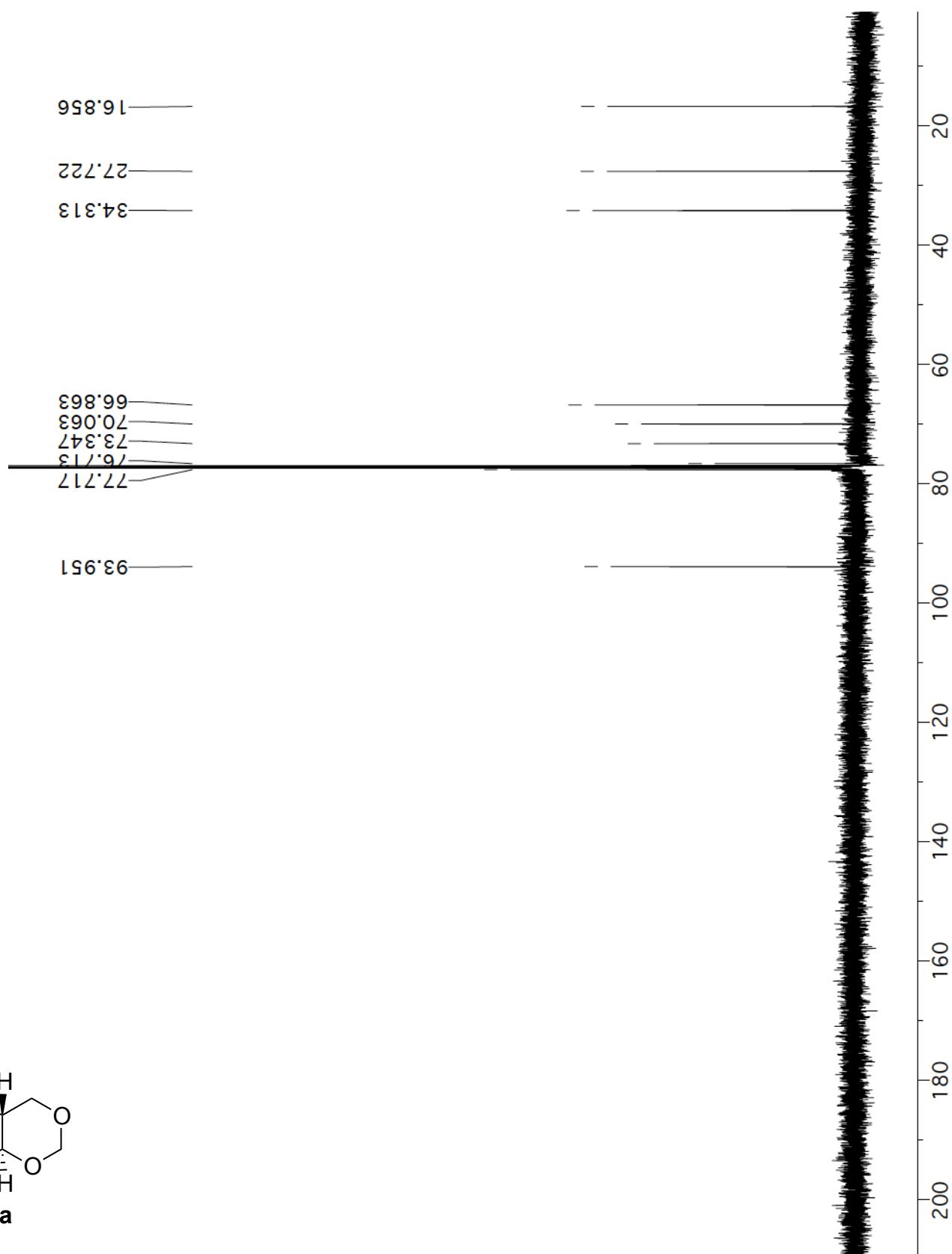


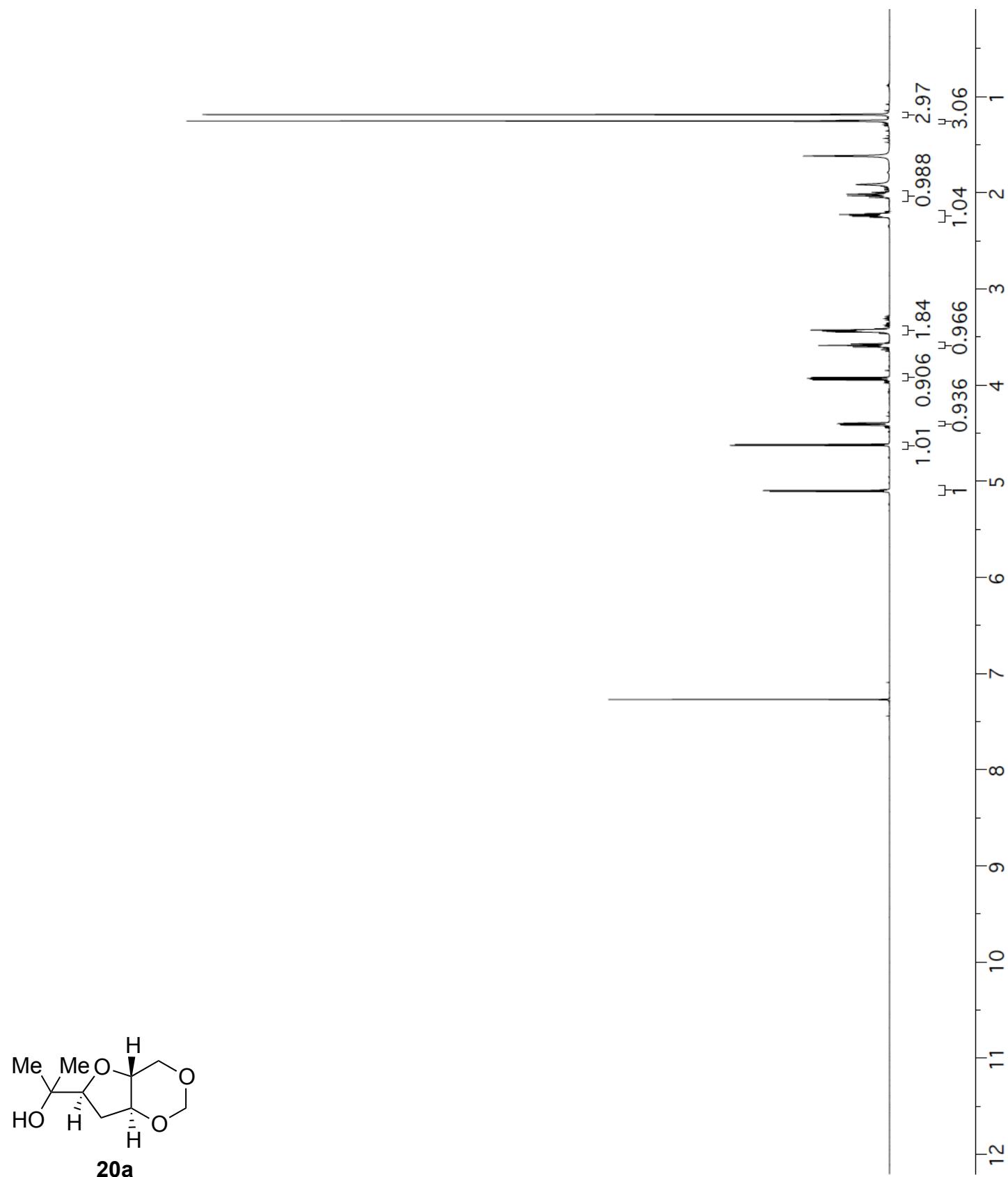


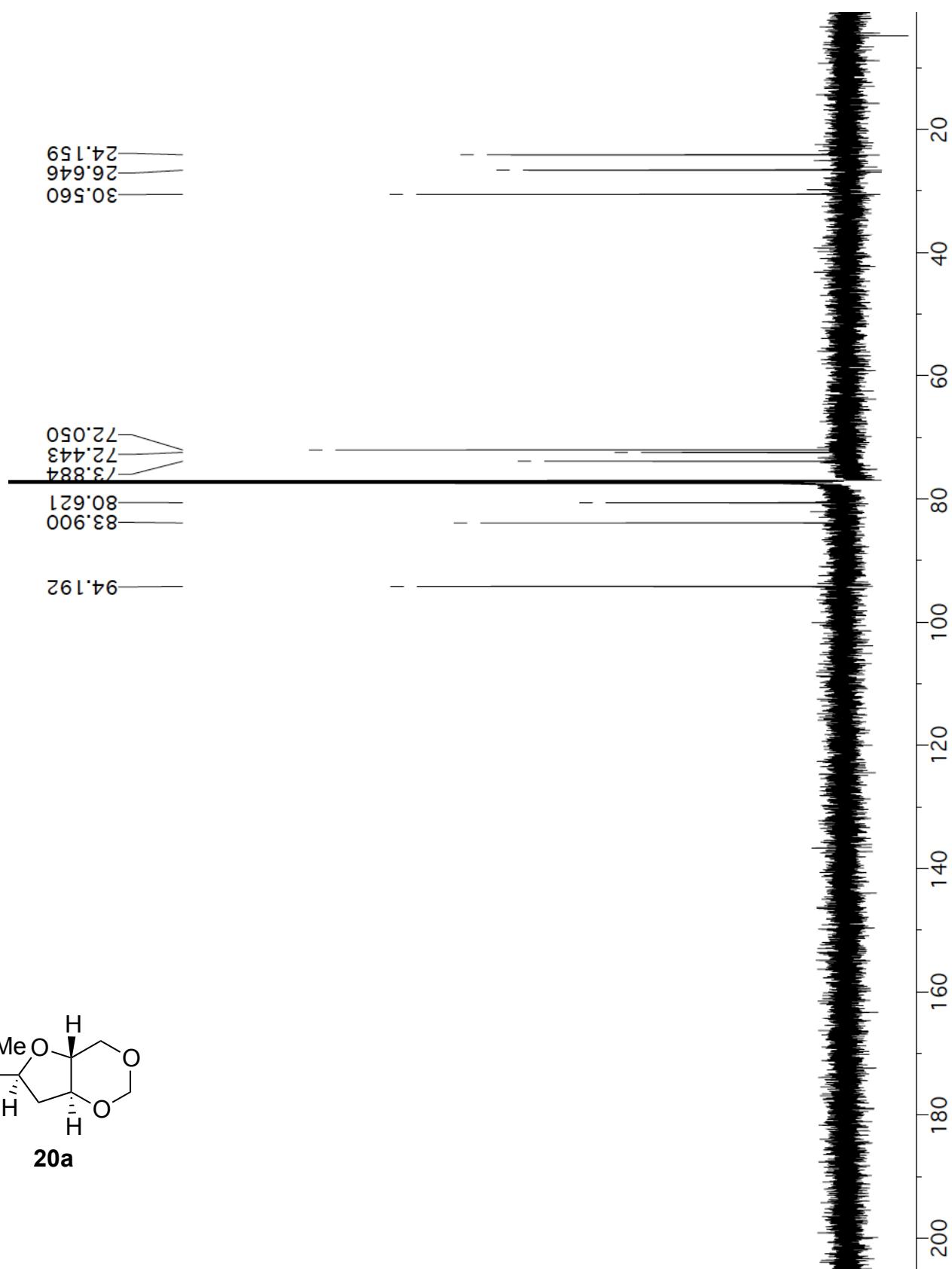


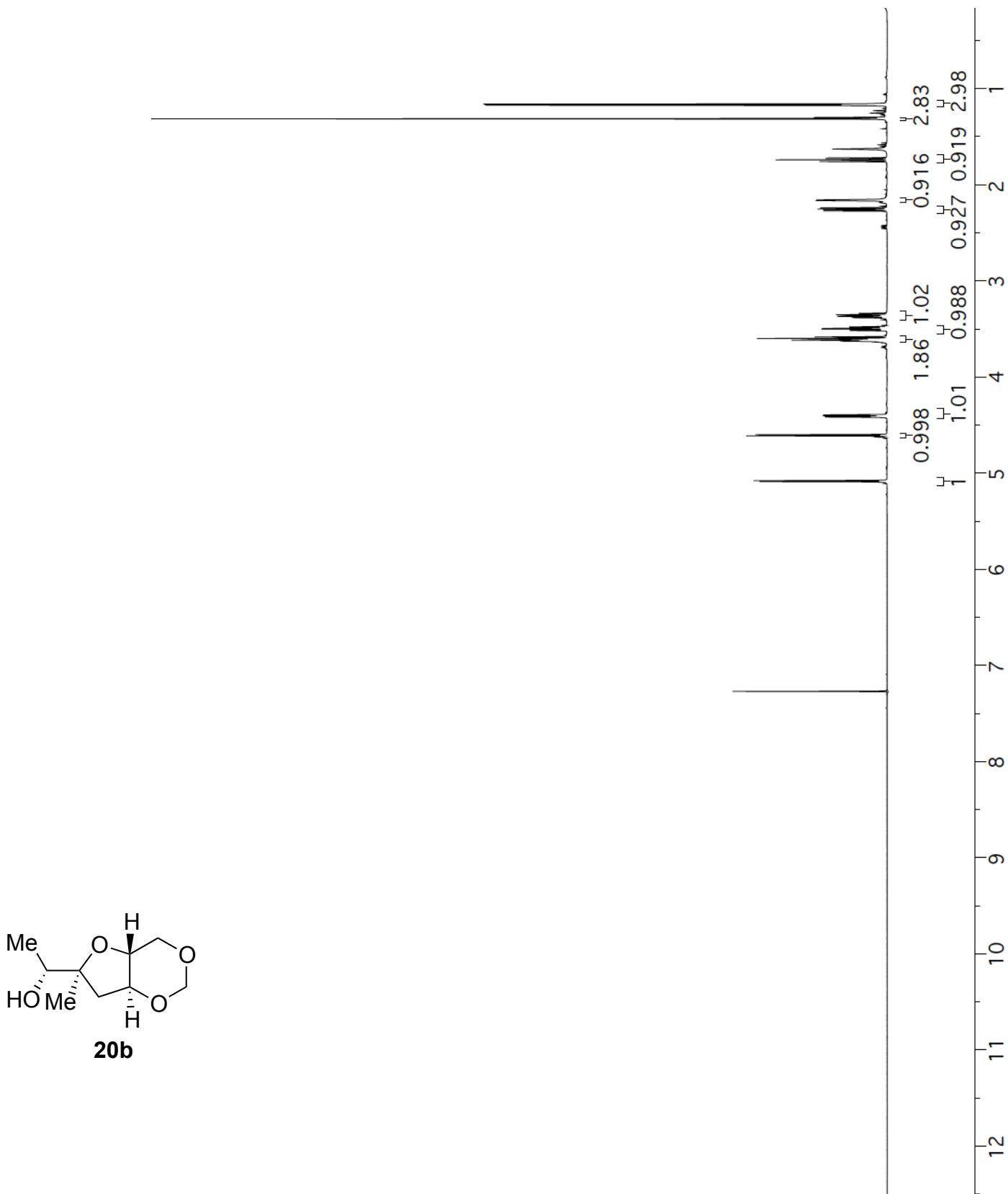


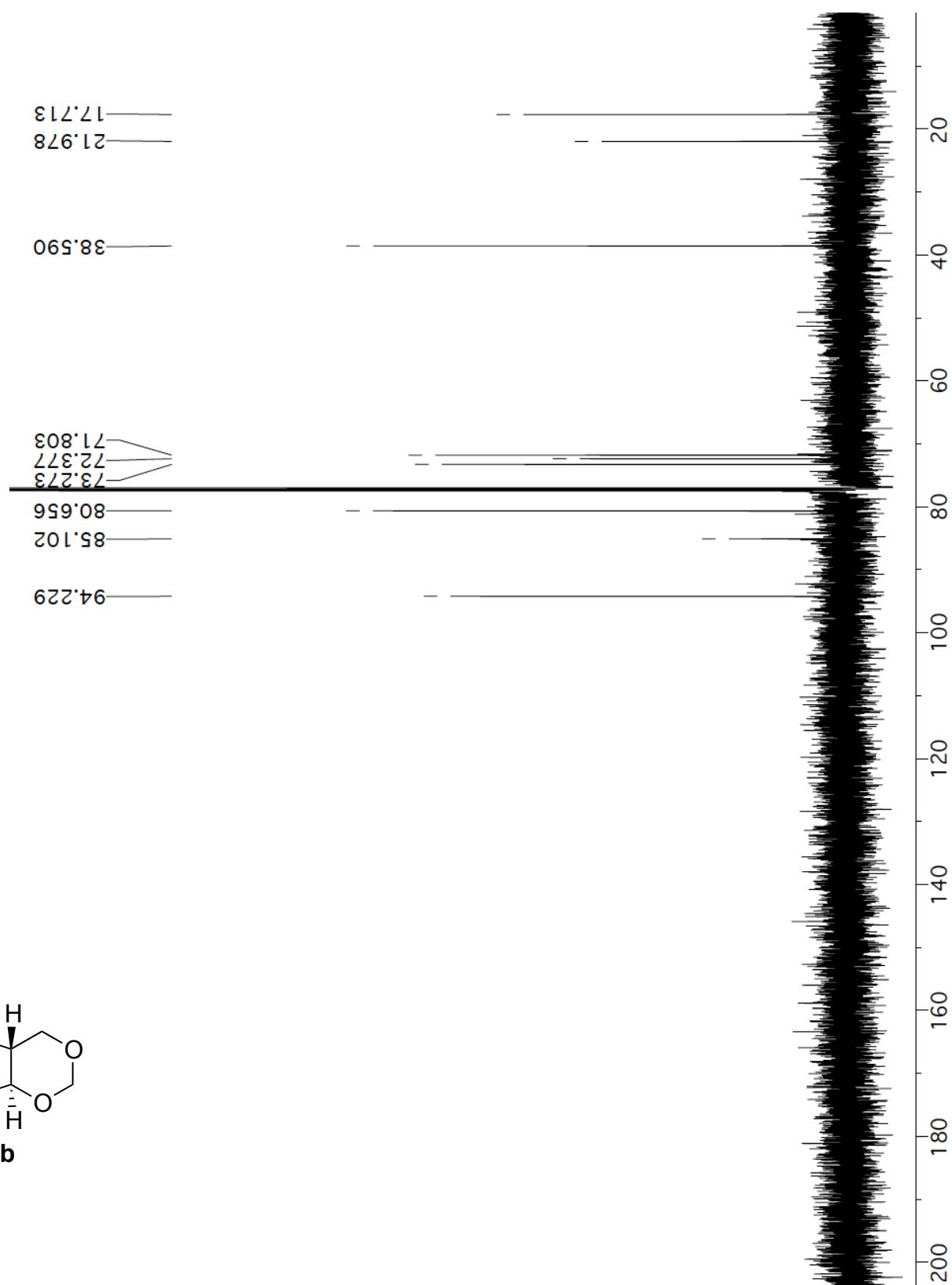


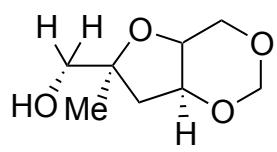
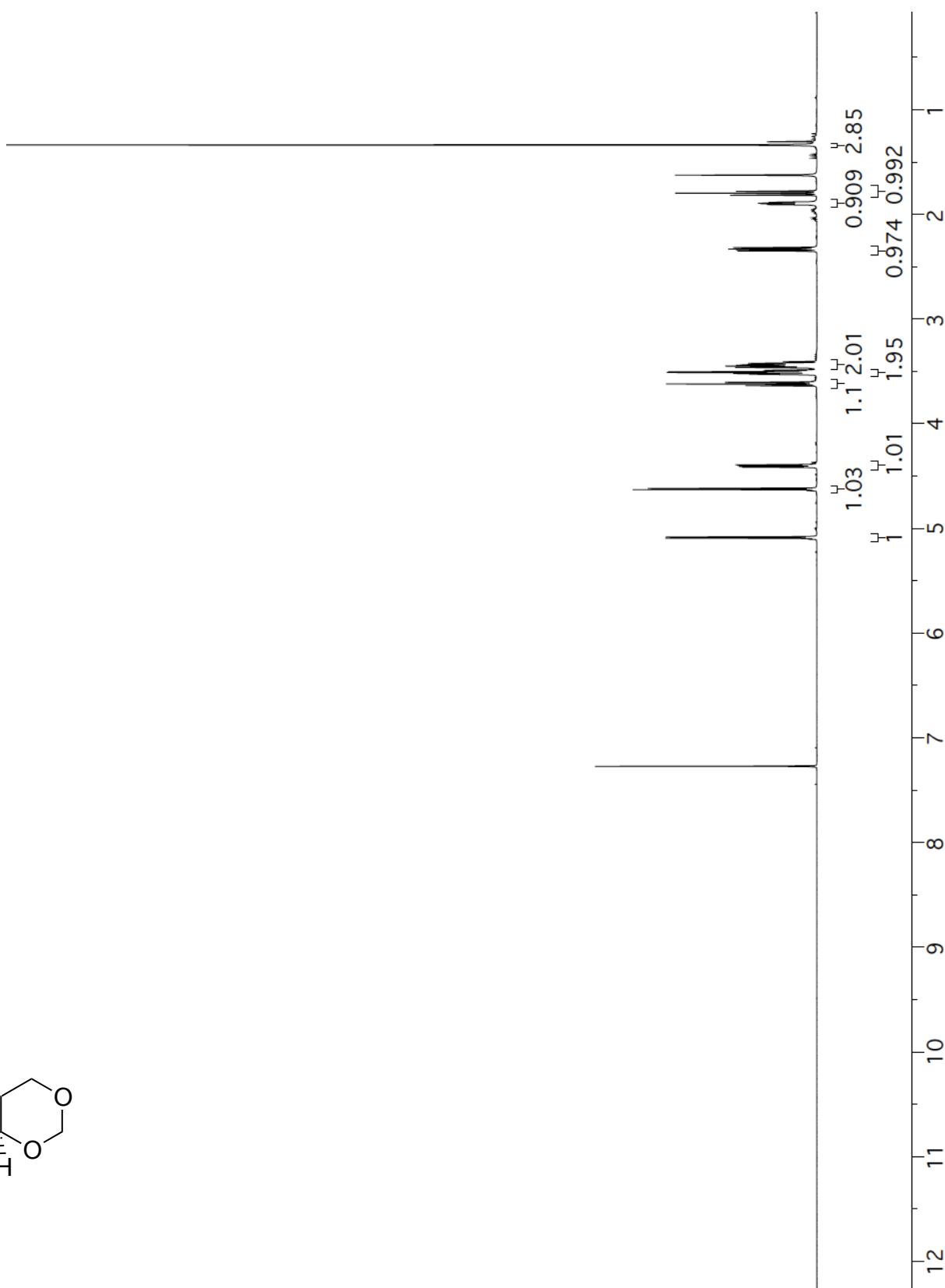




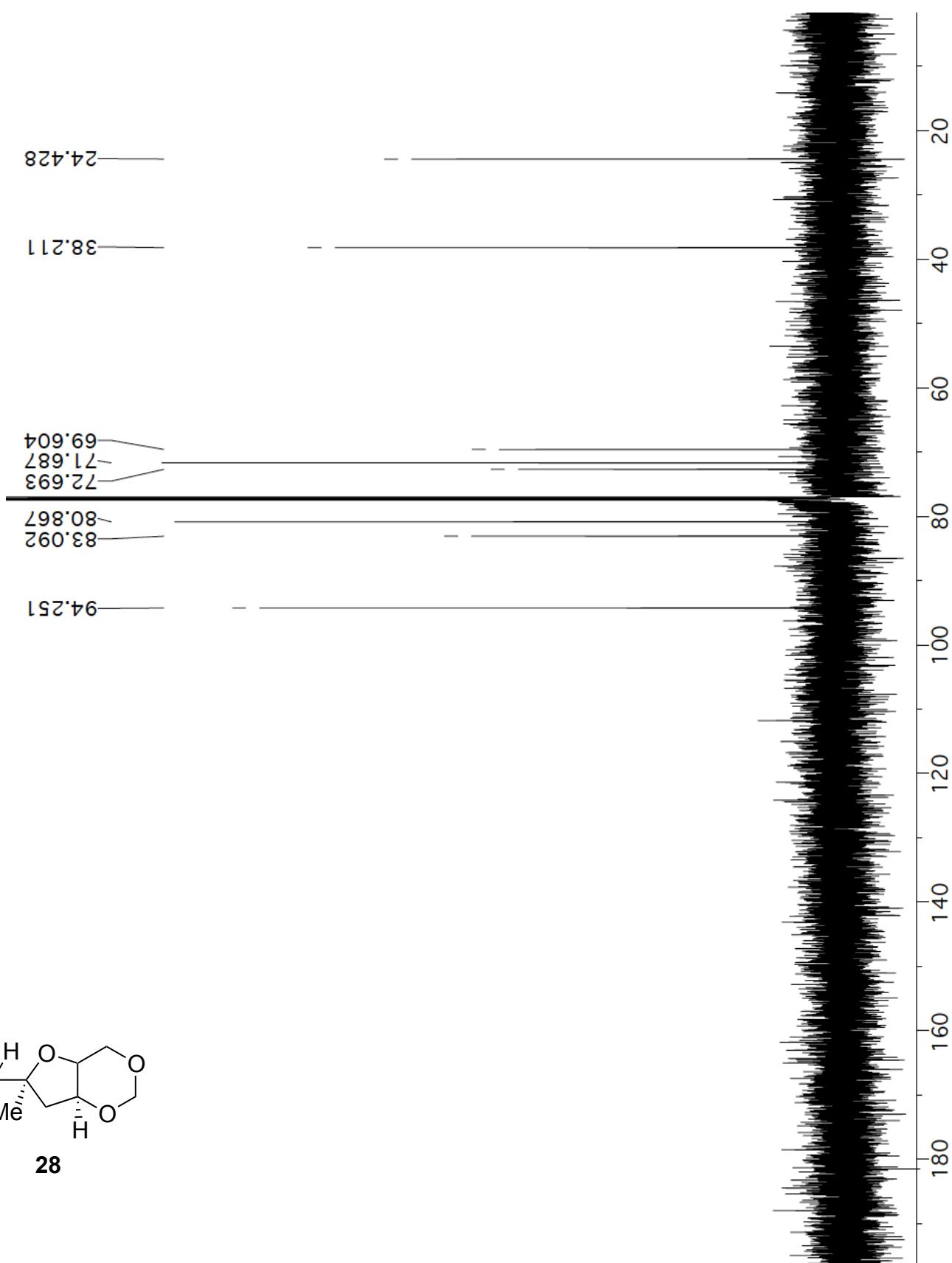


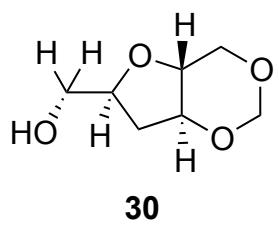
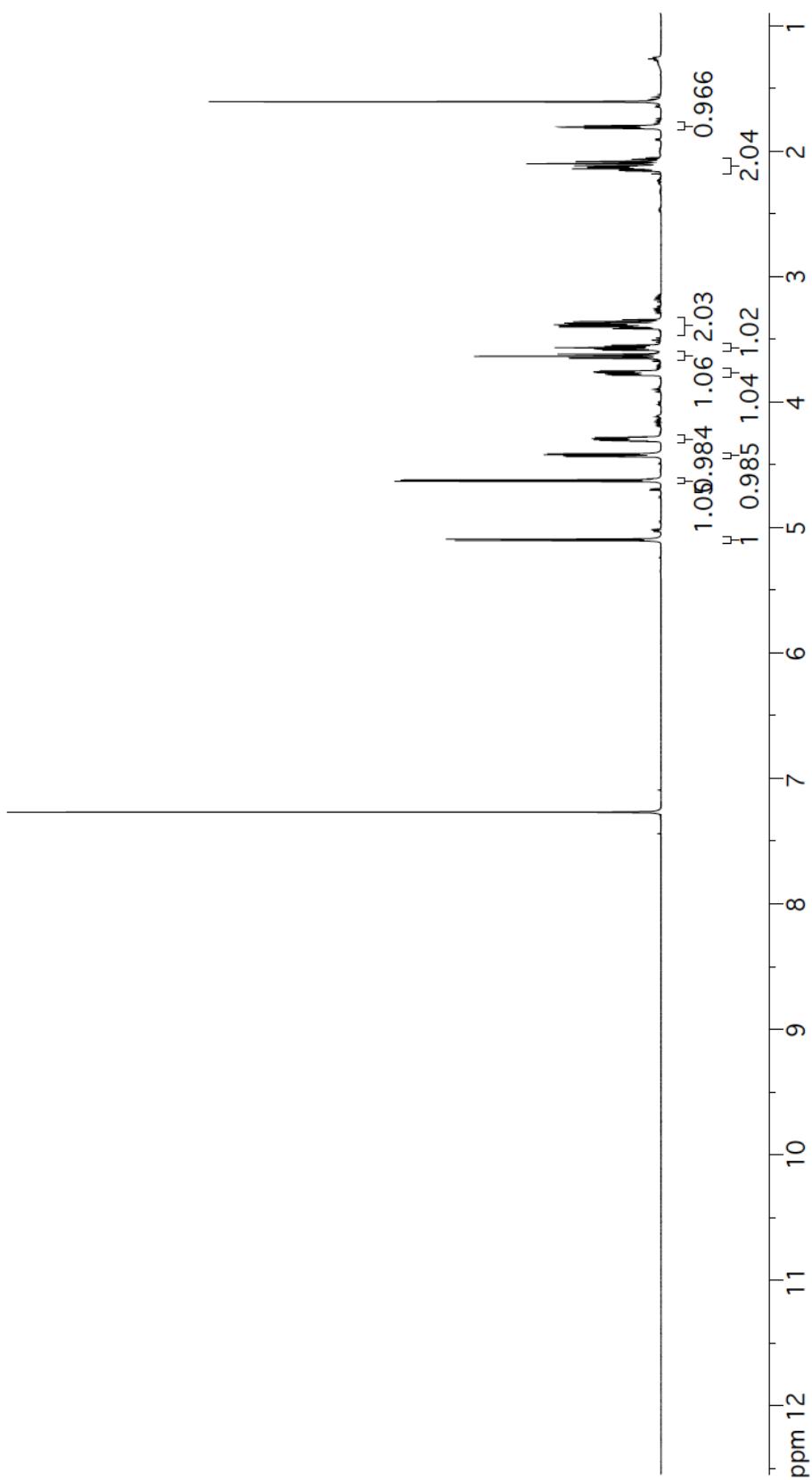


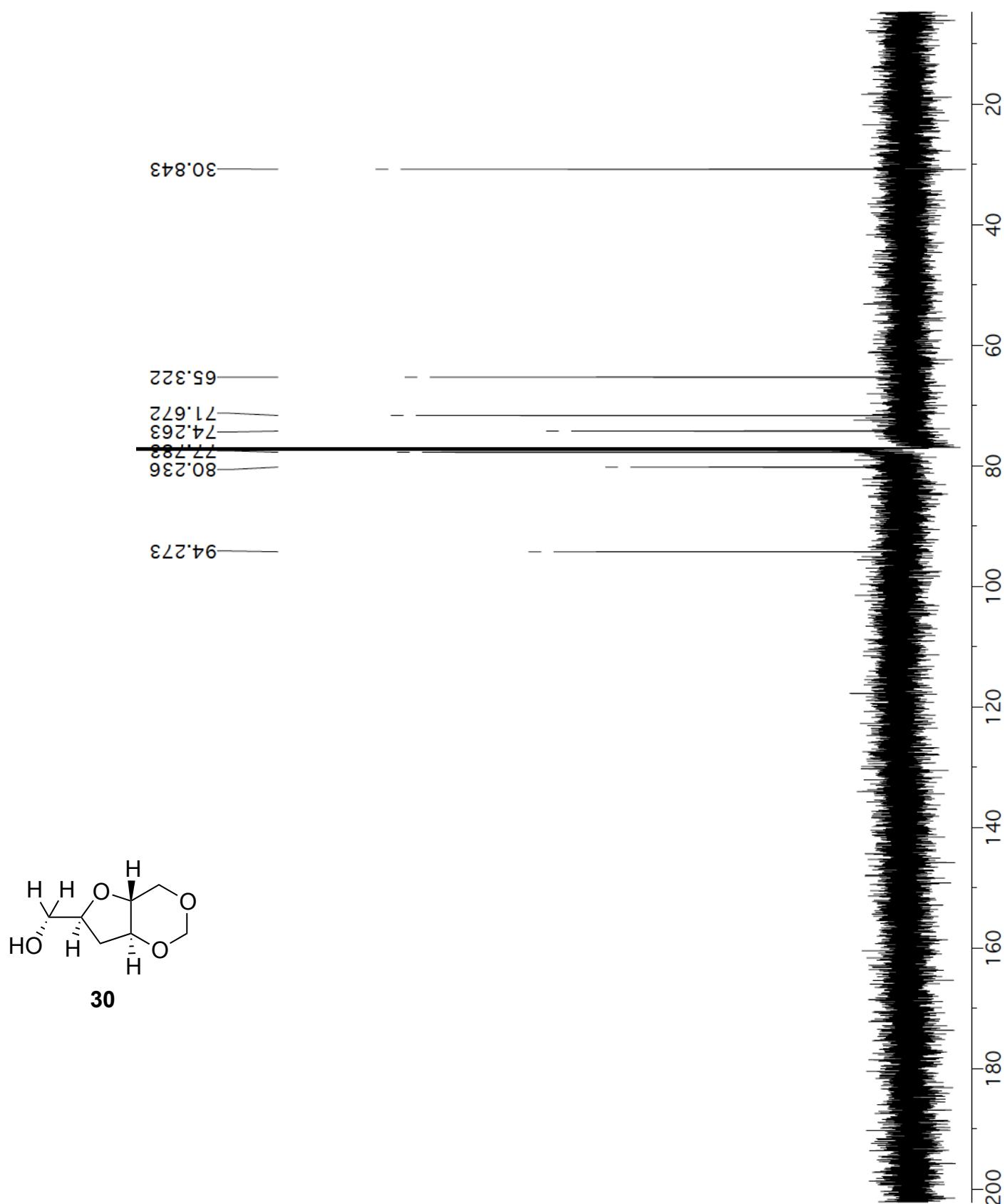


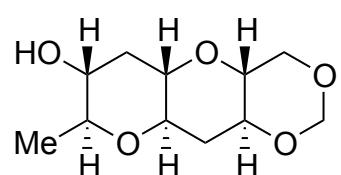


**28**

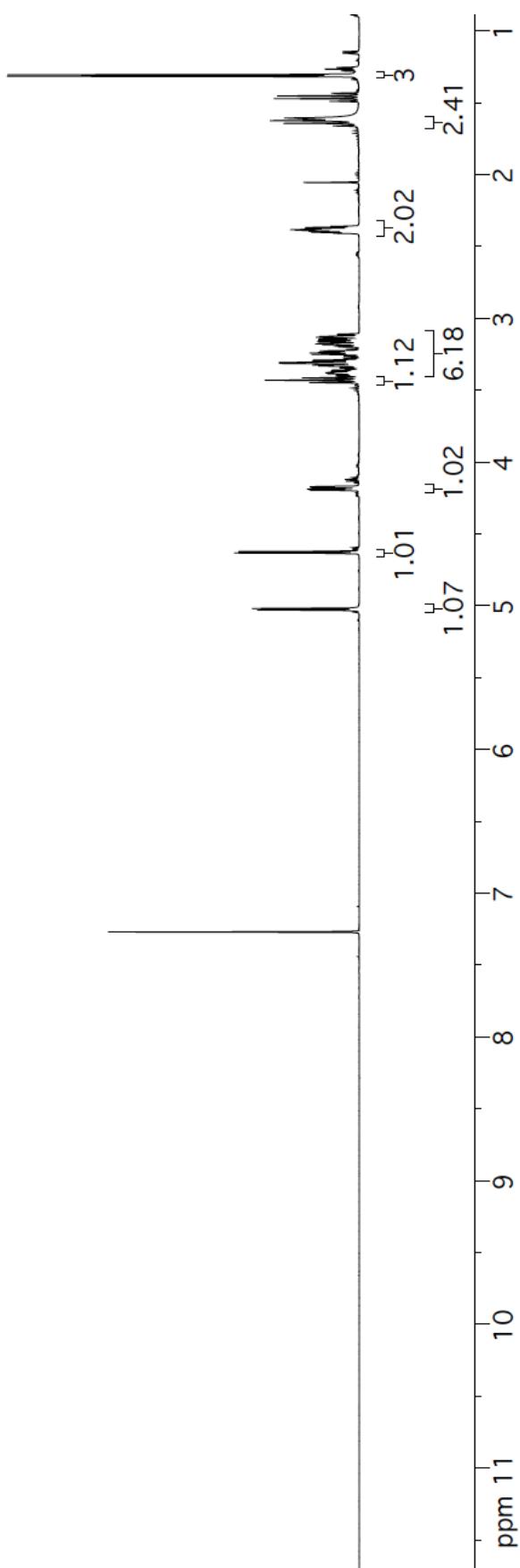


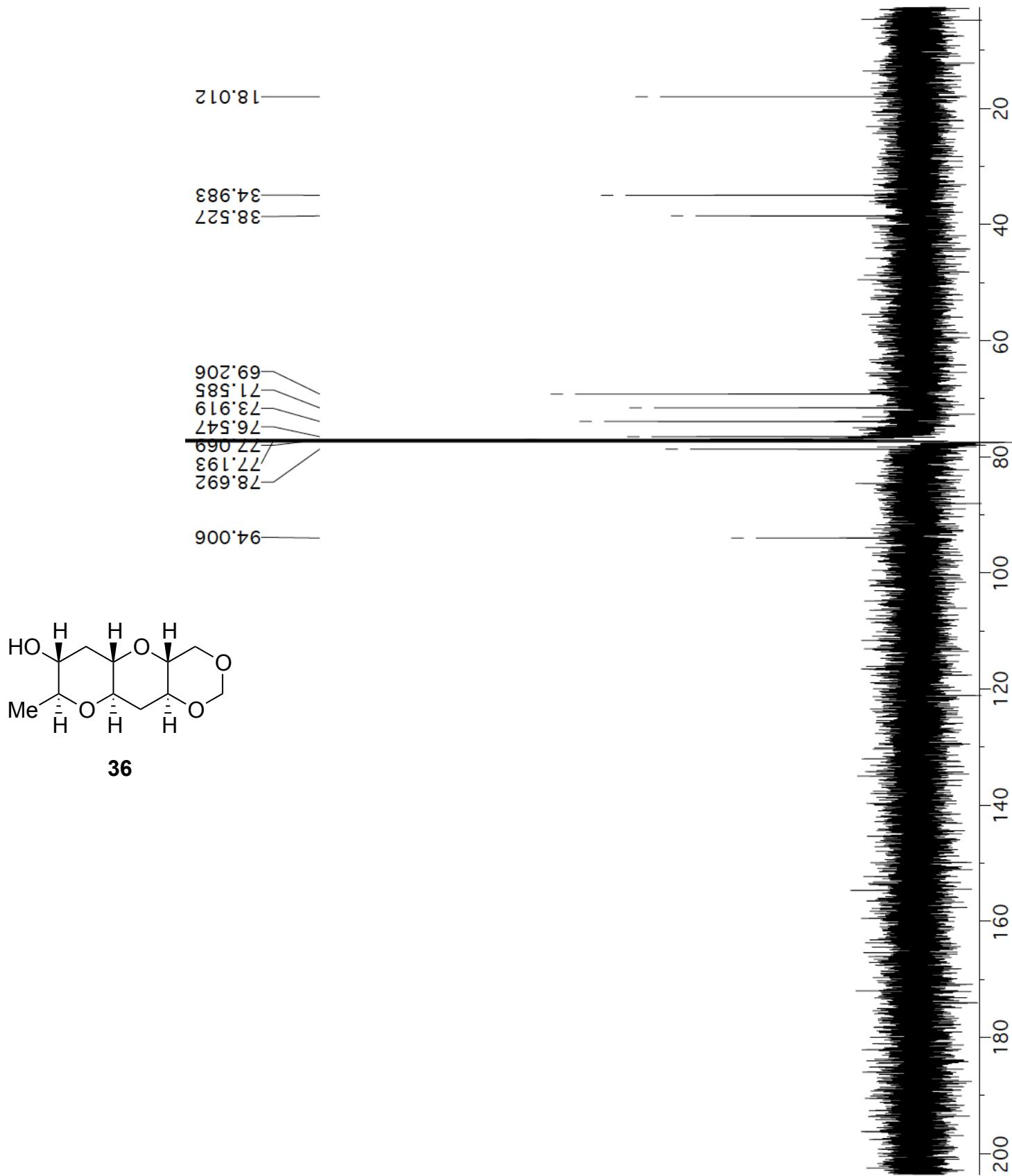


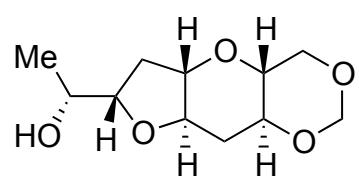




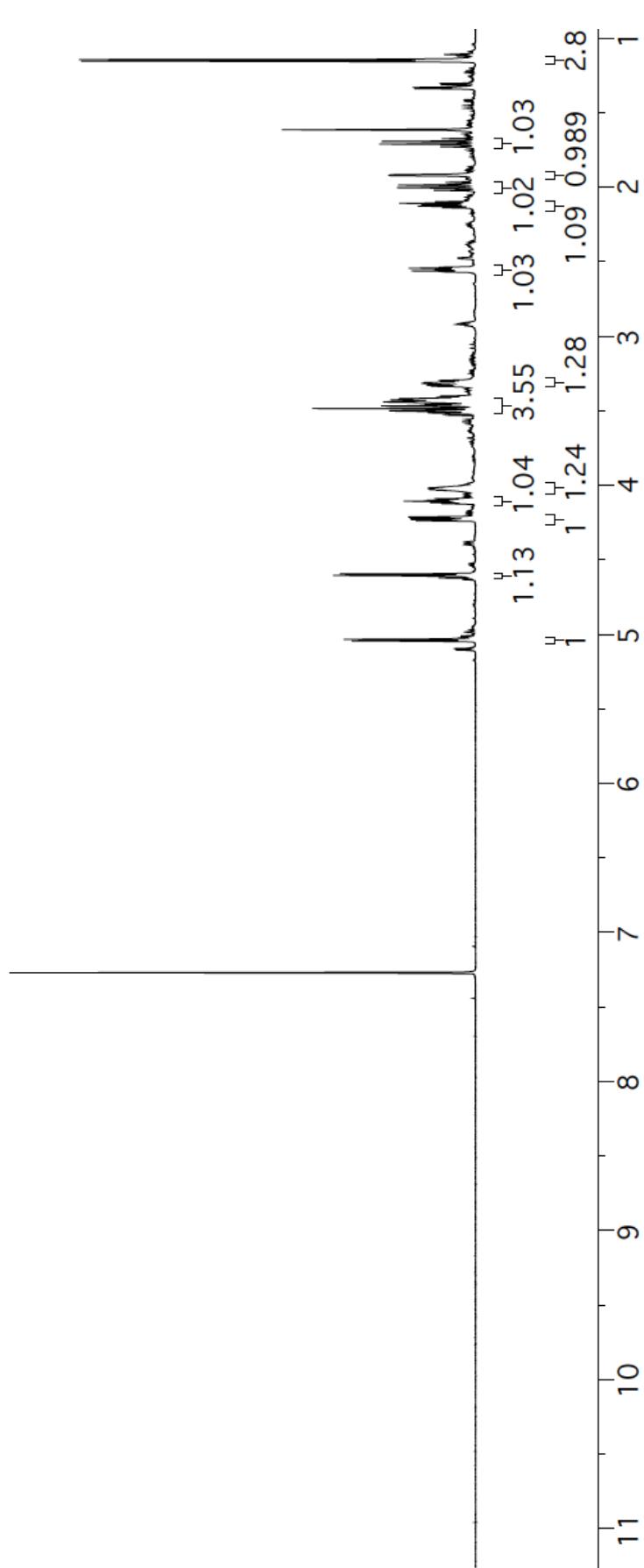
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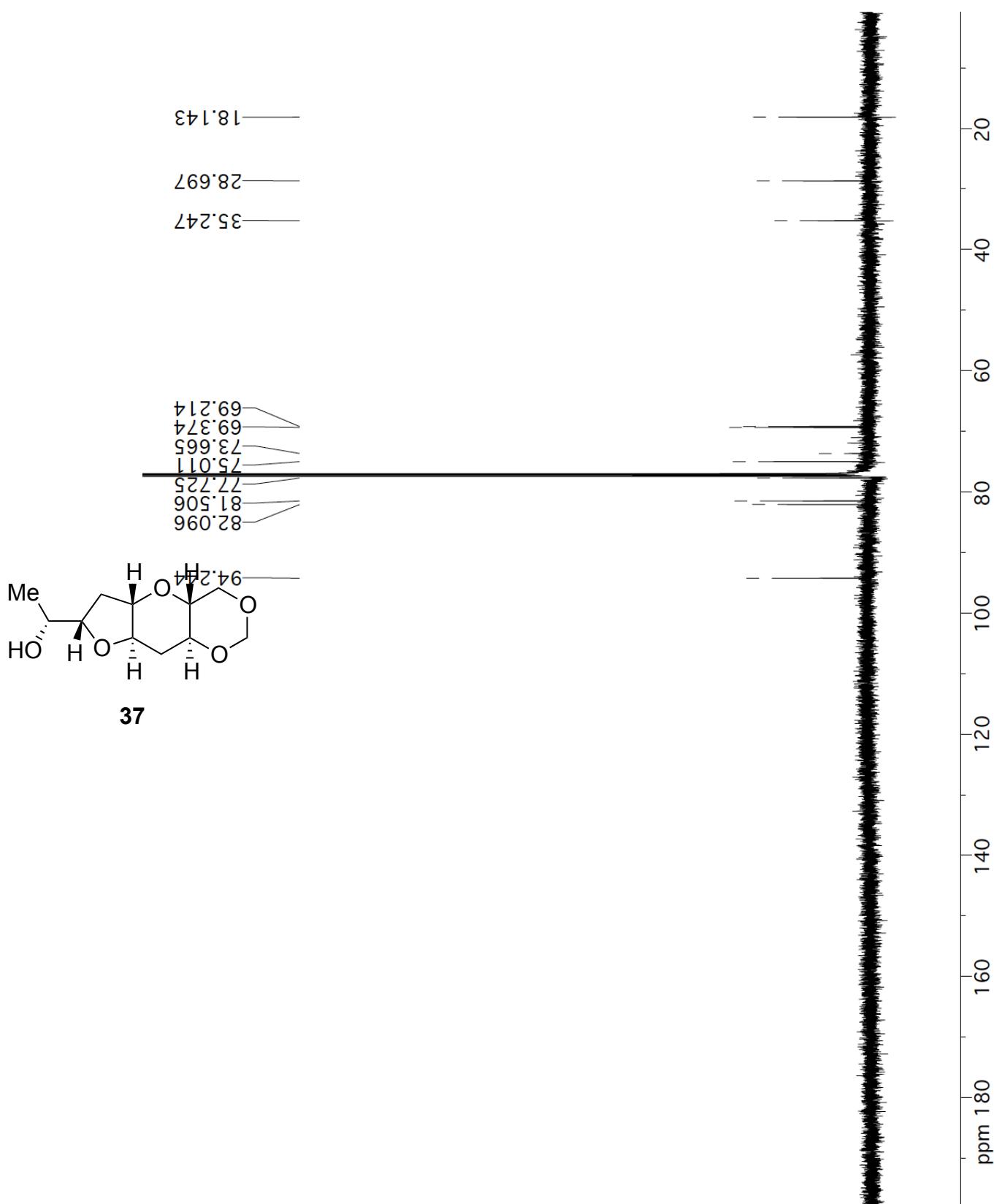


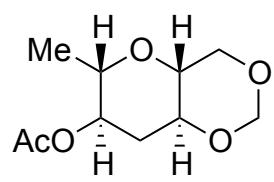
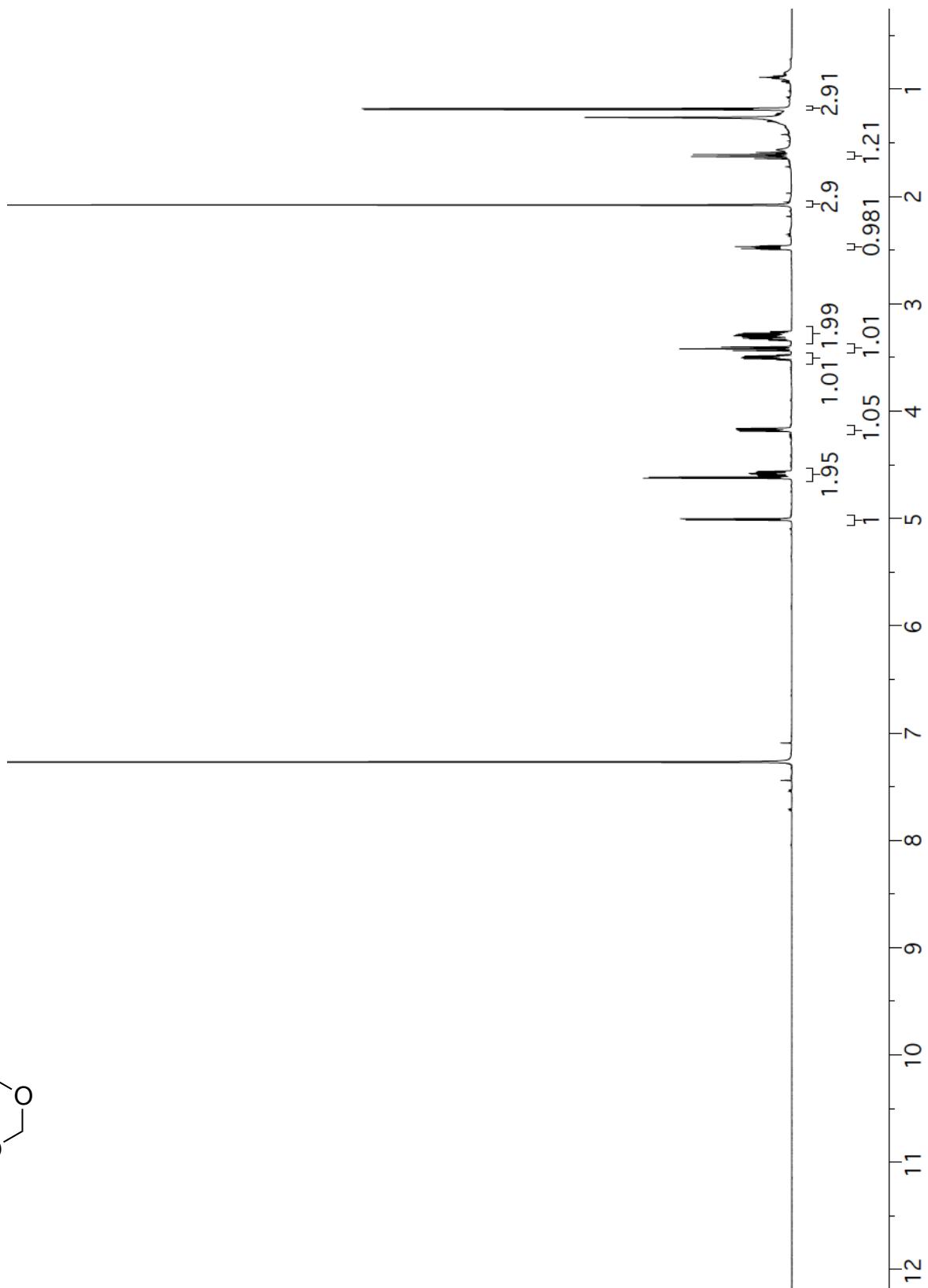


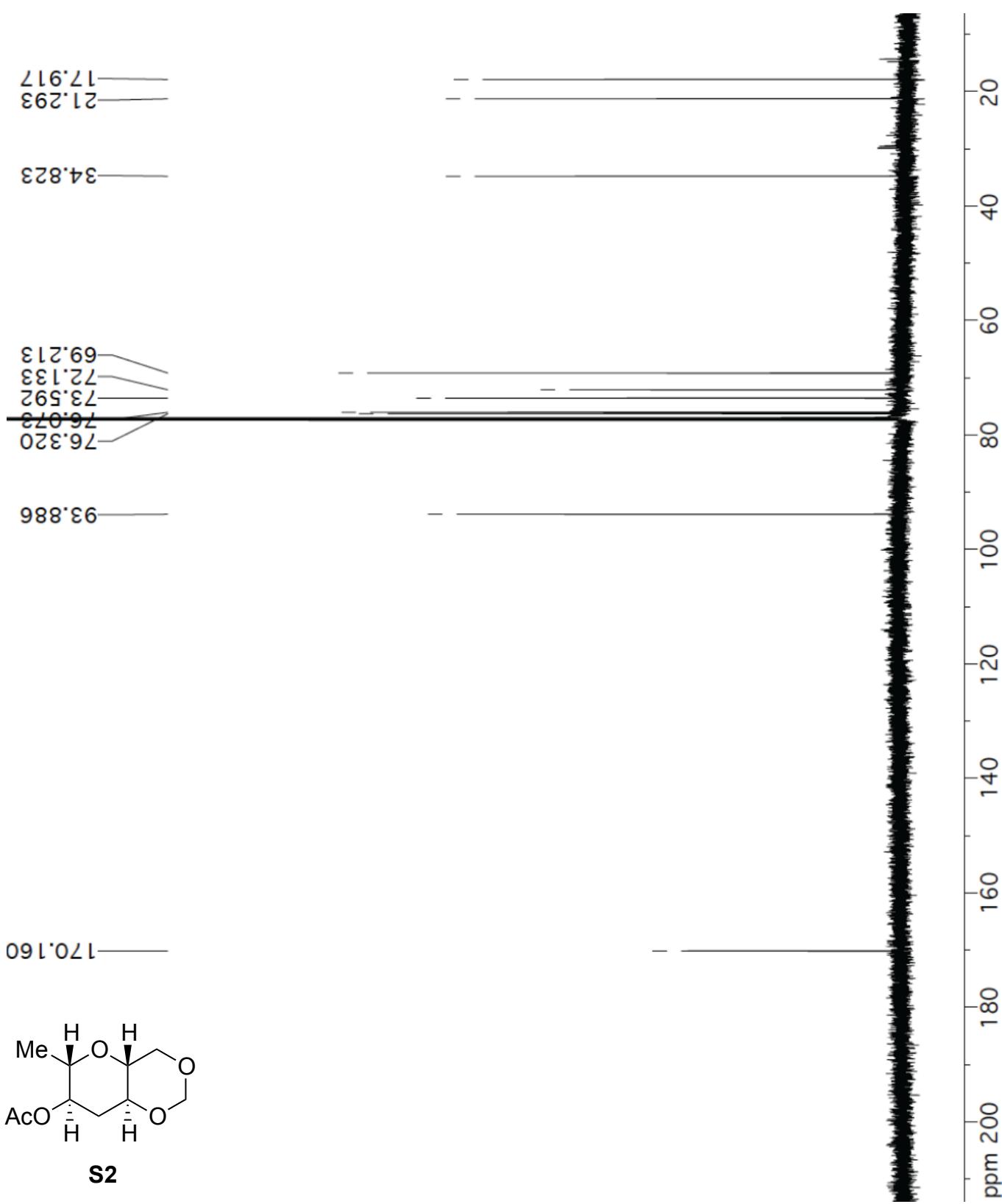


37

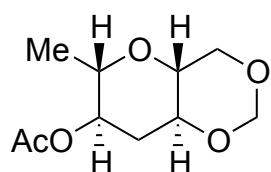




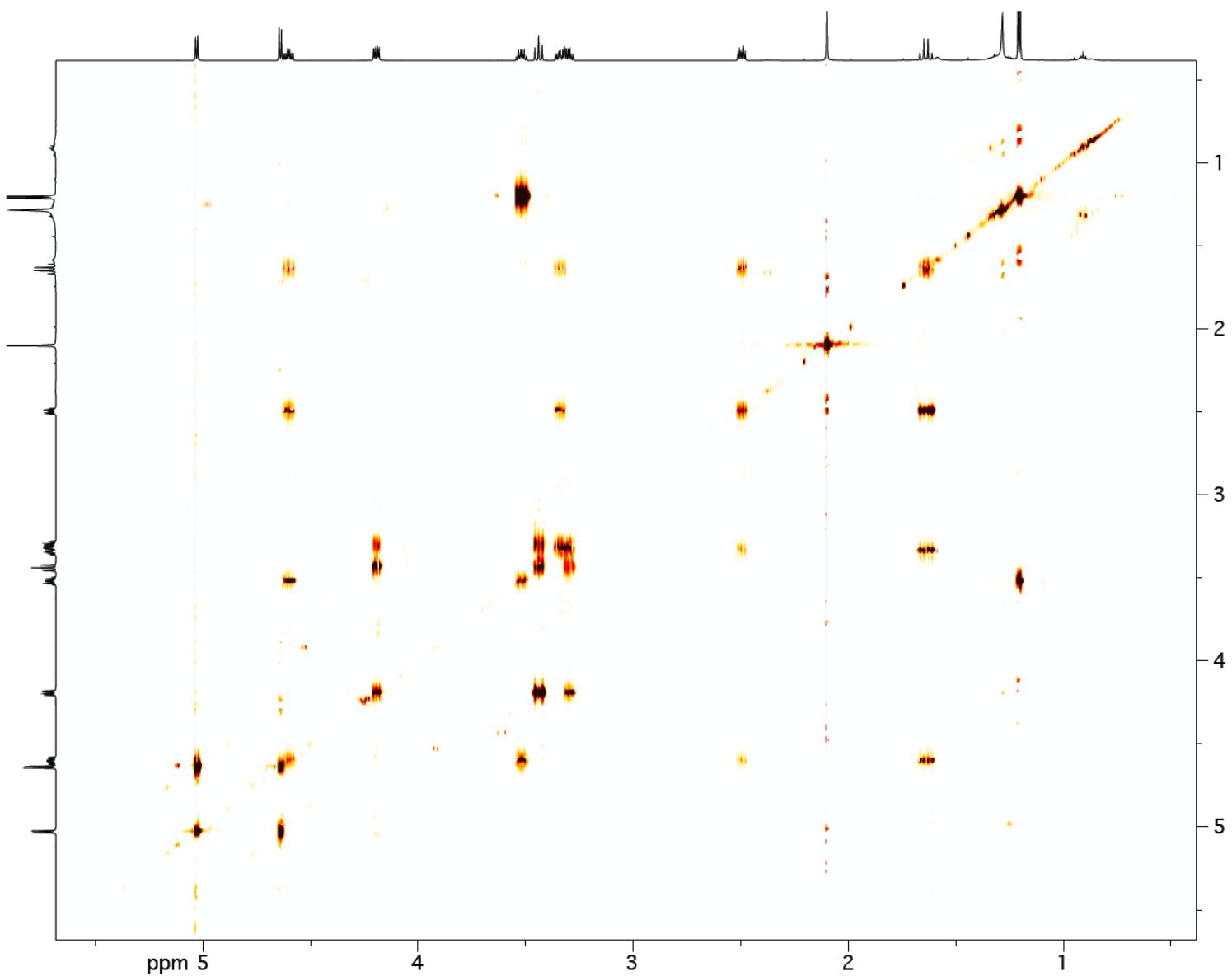


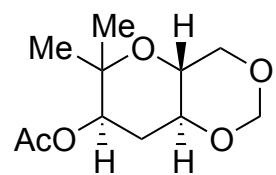


**S2 gCOSY**

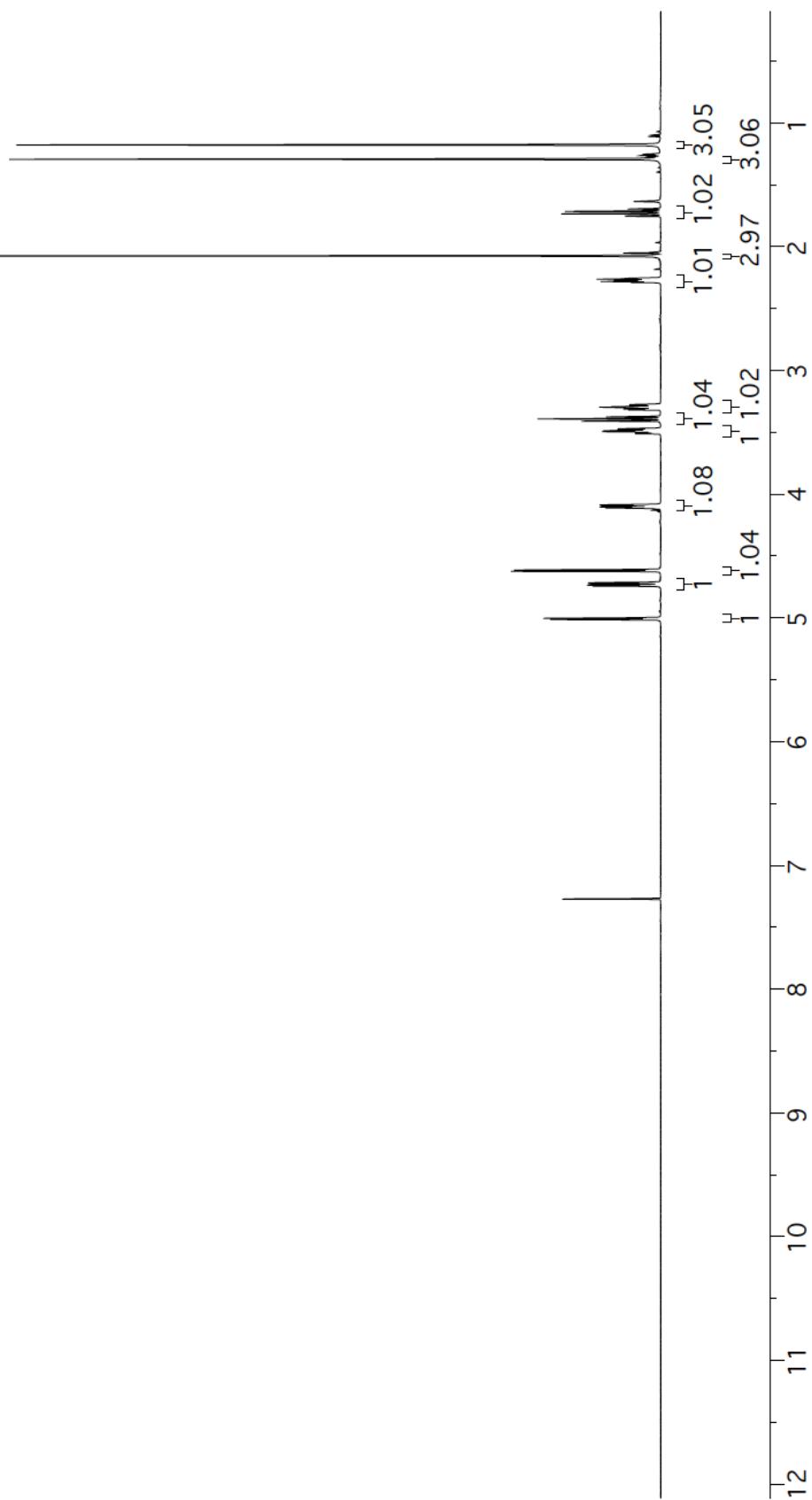


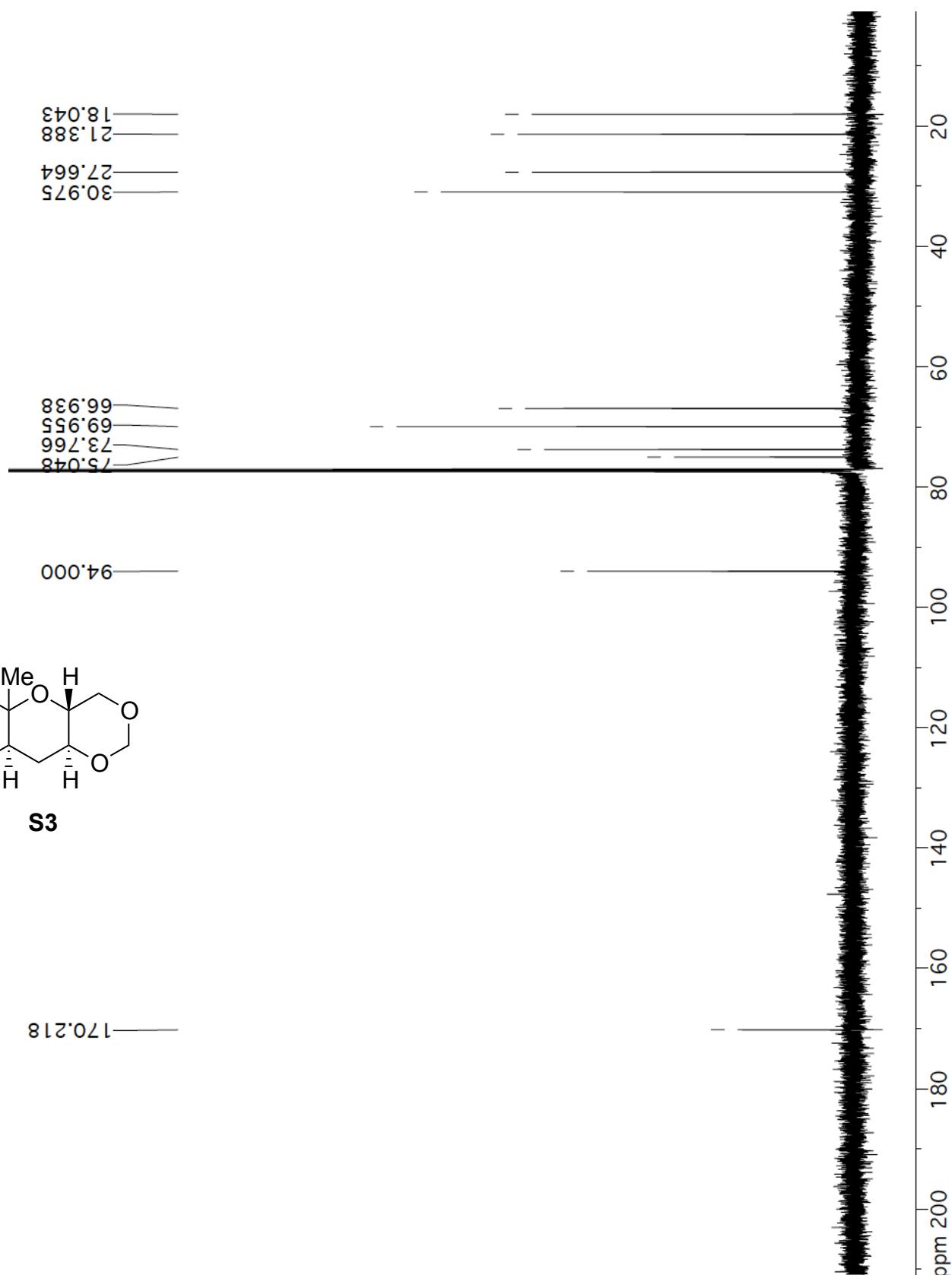
**S2**



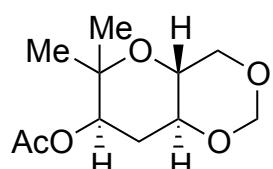


S3

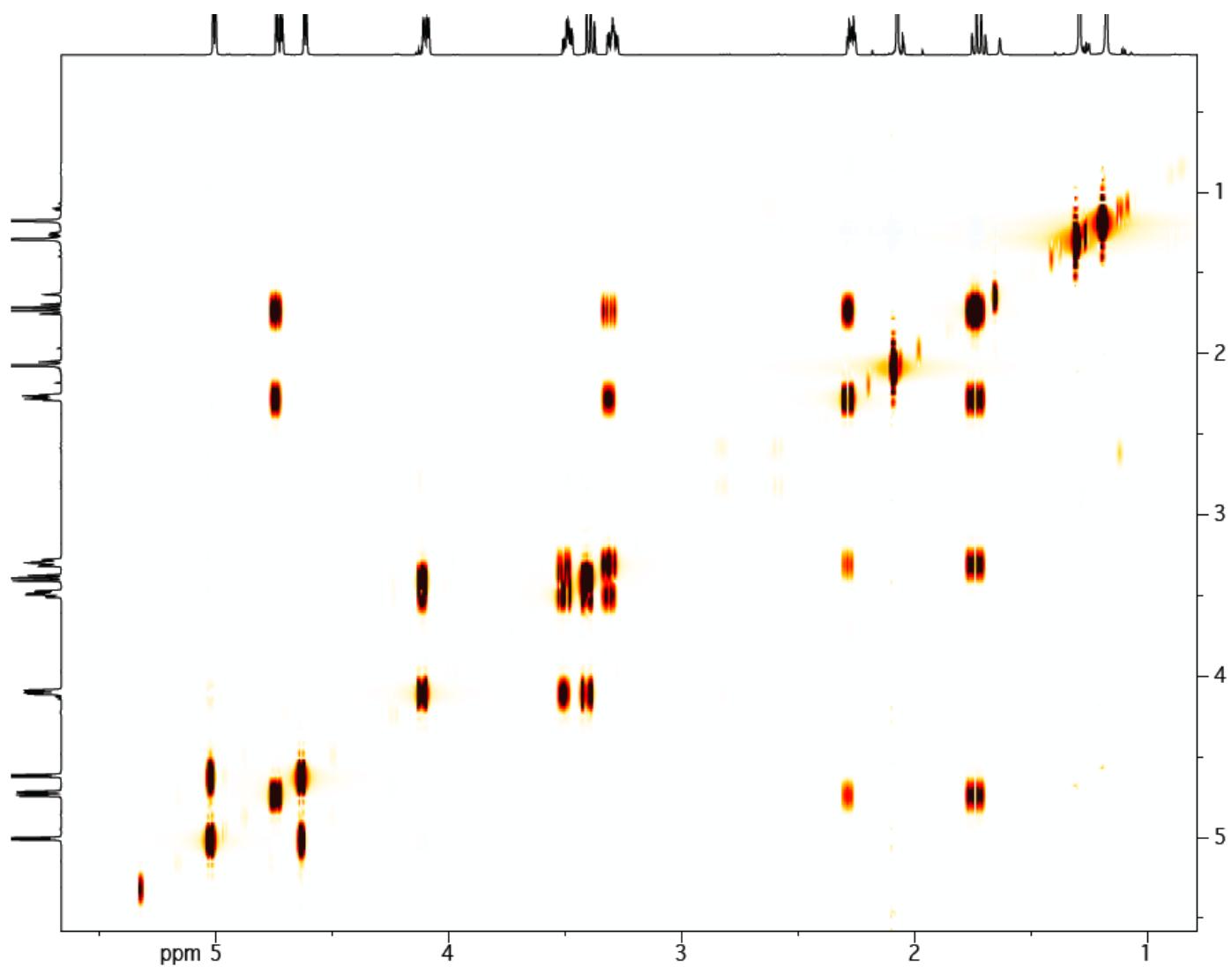


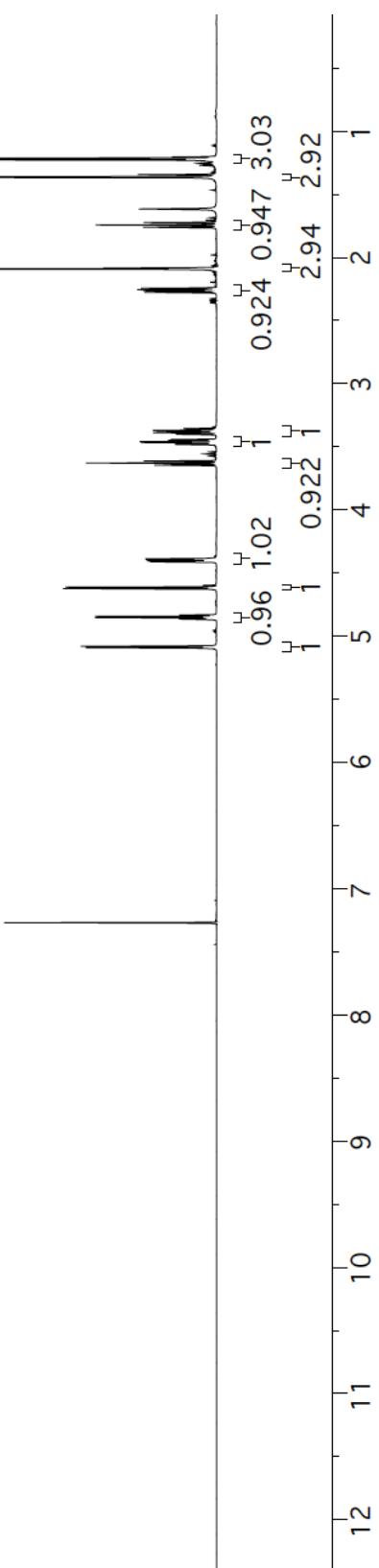
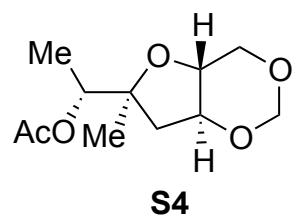


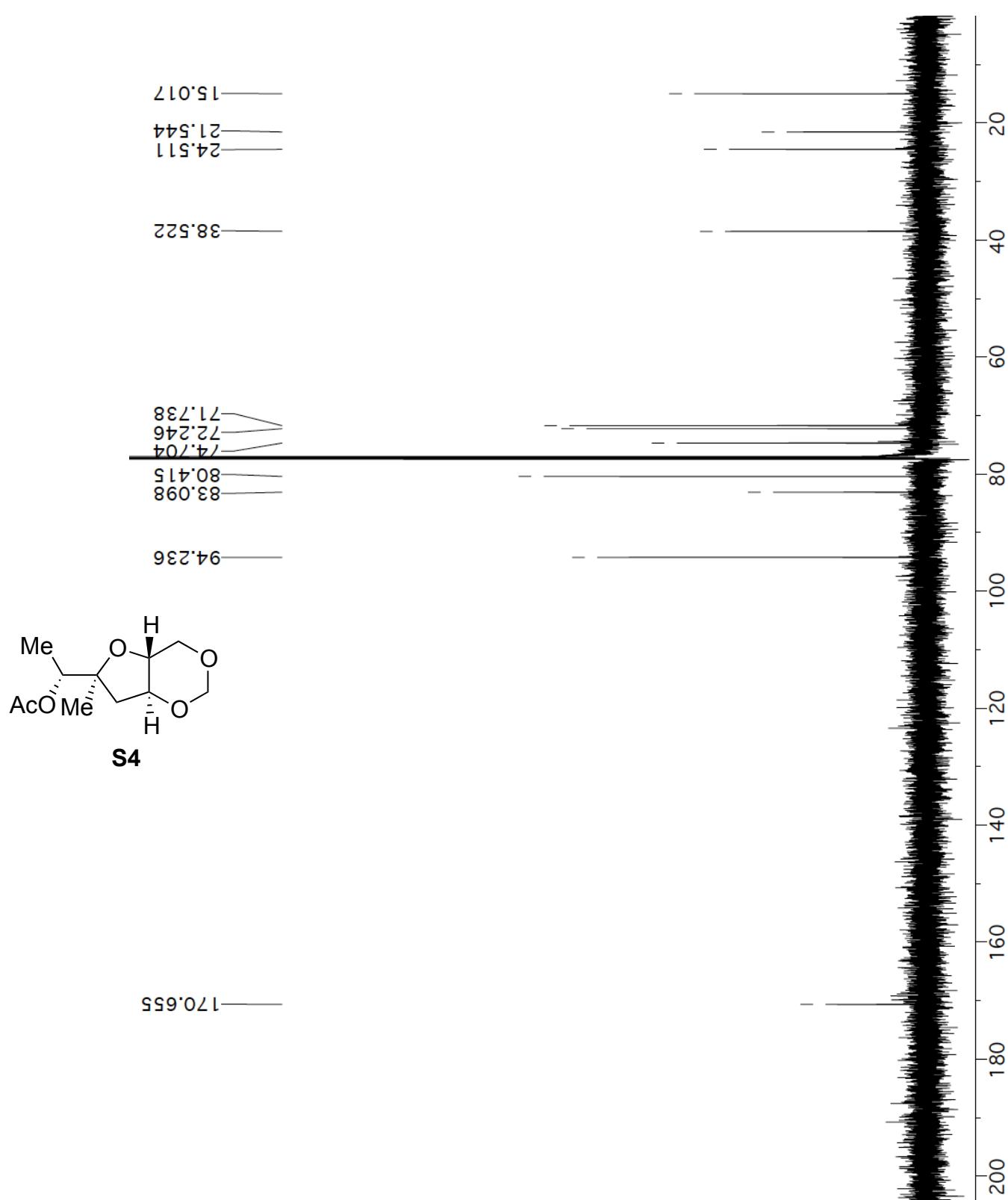
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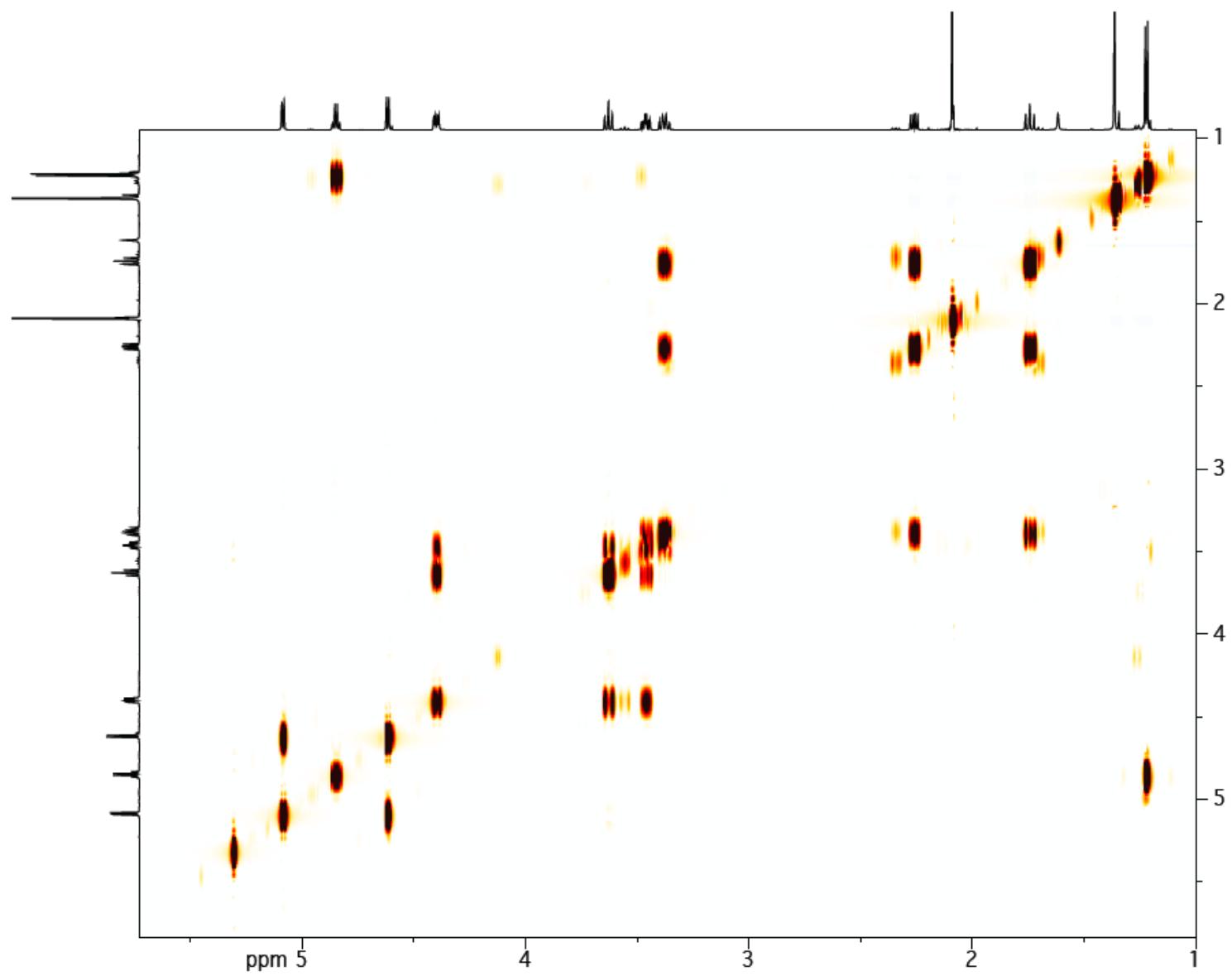
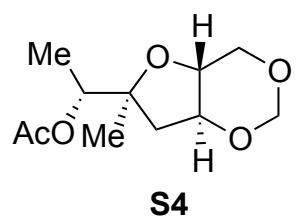
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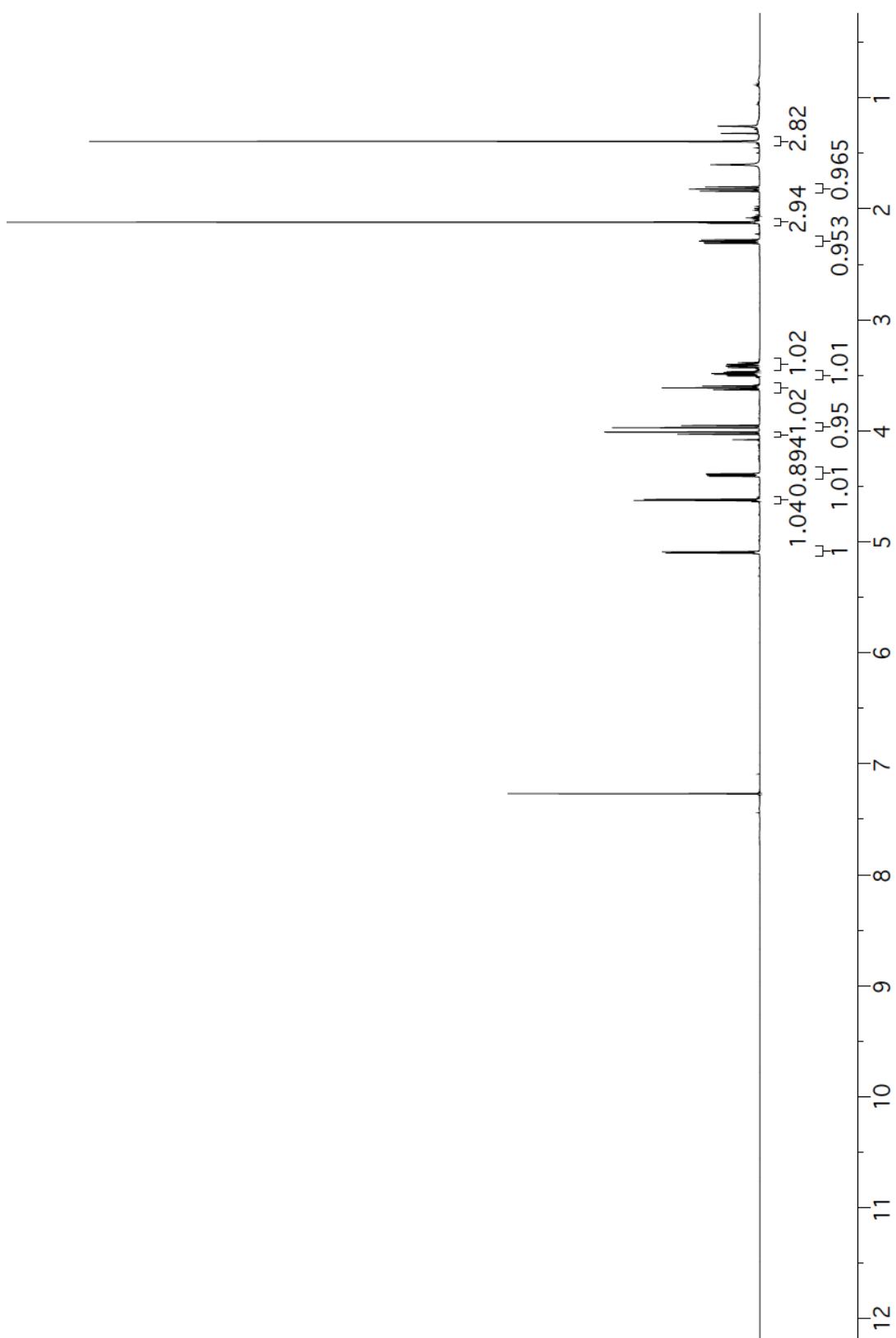
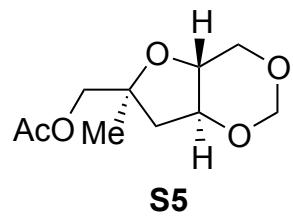


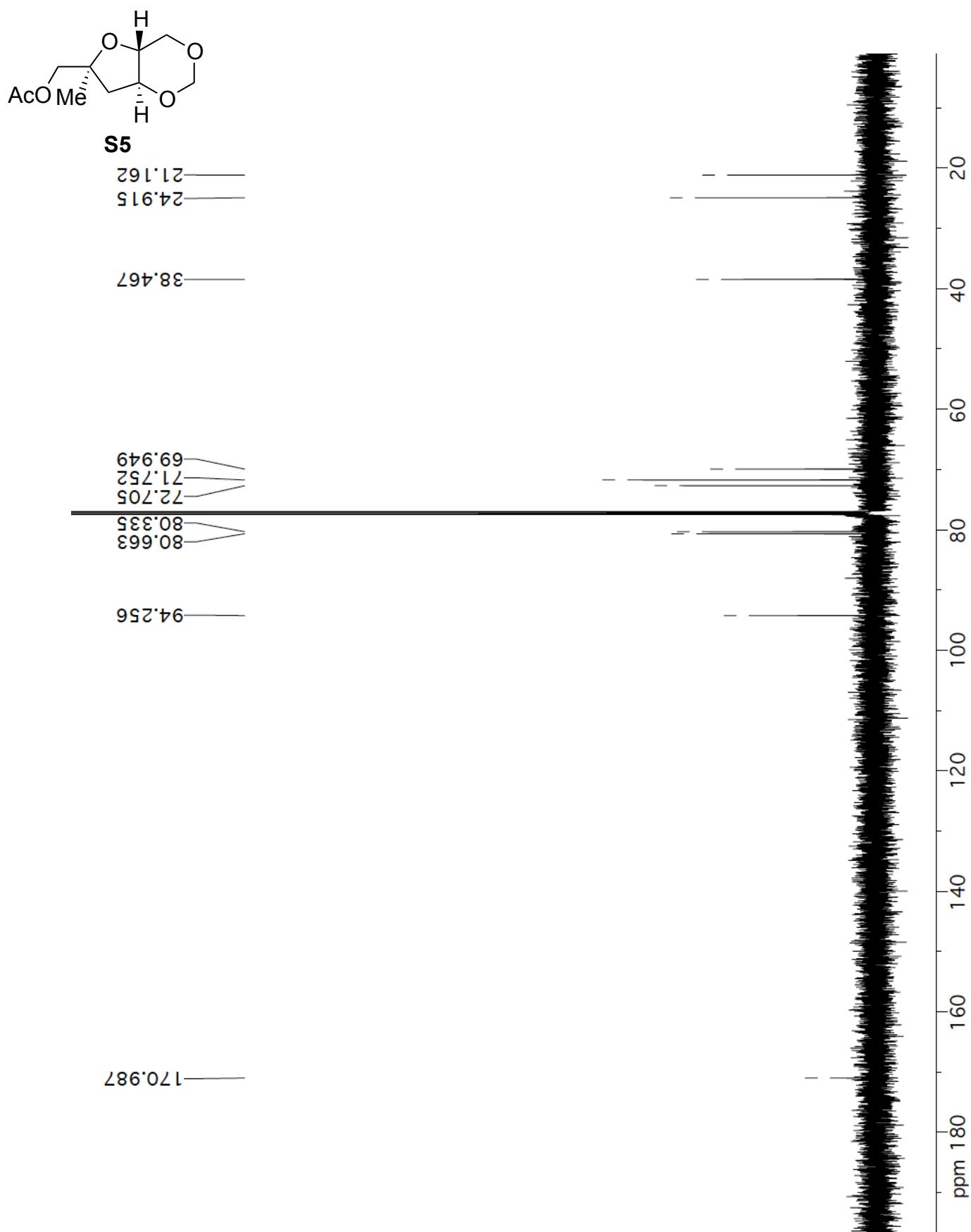




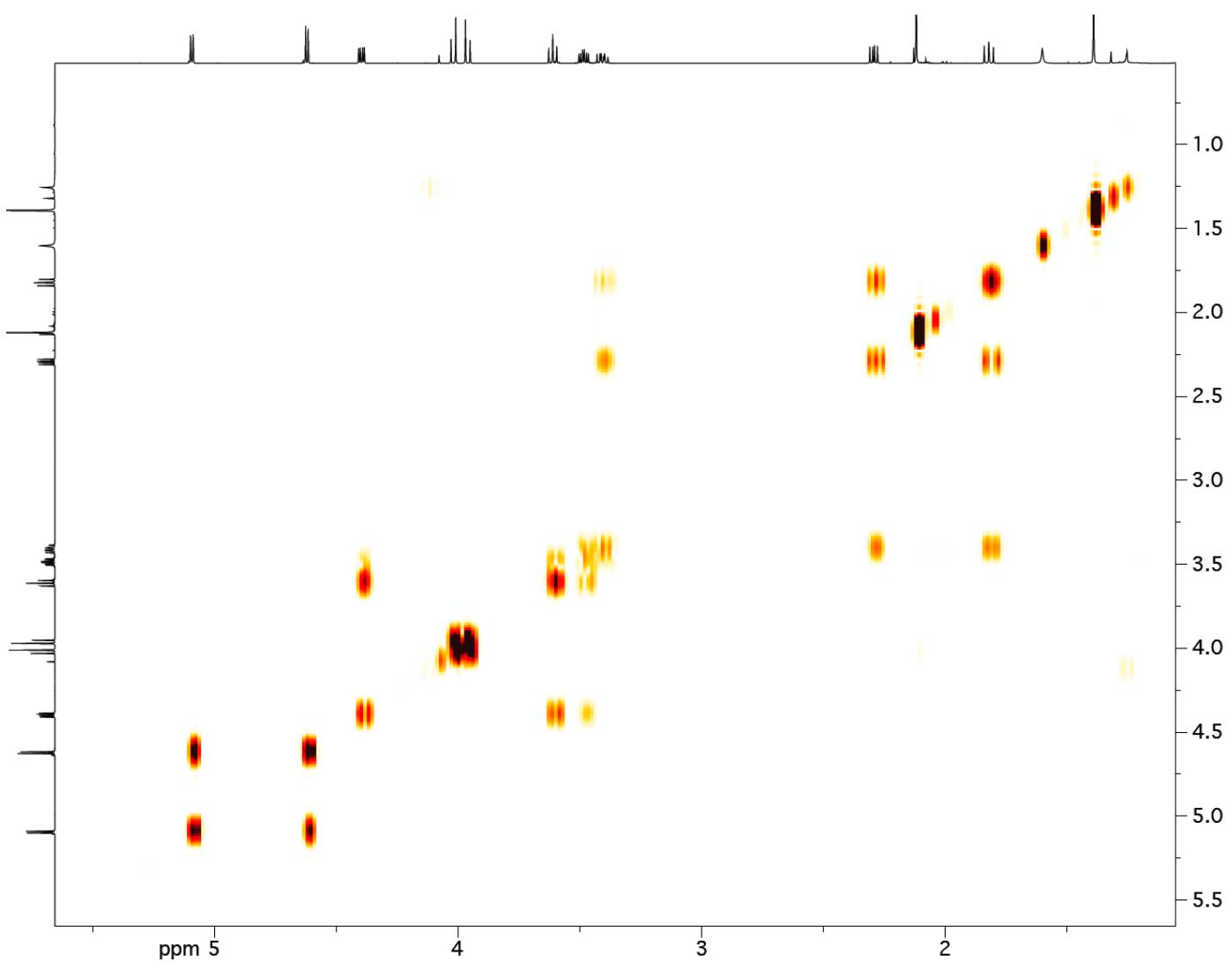
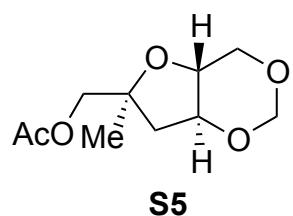
**S4 gCOSY**

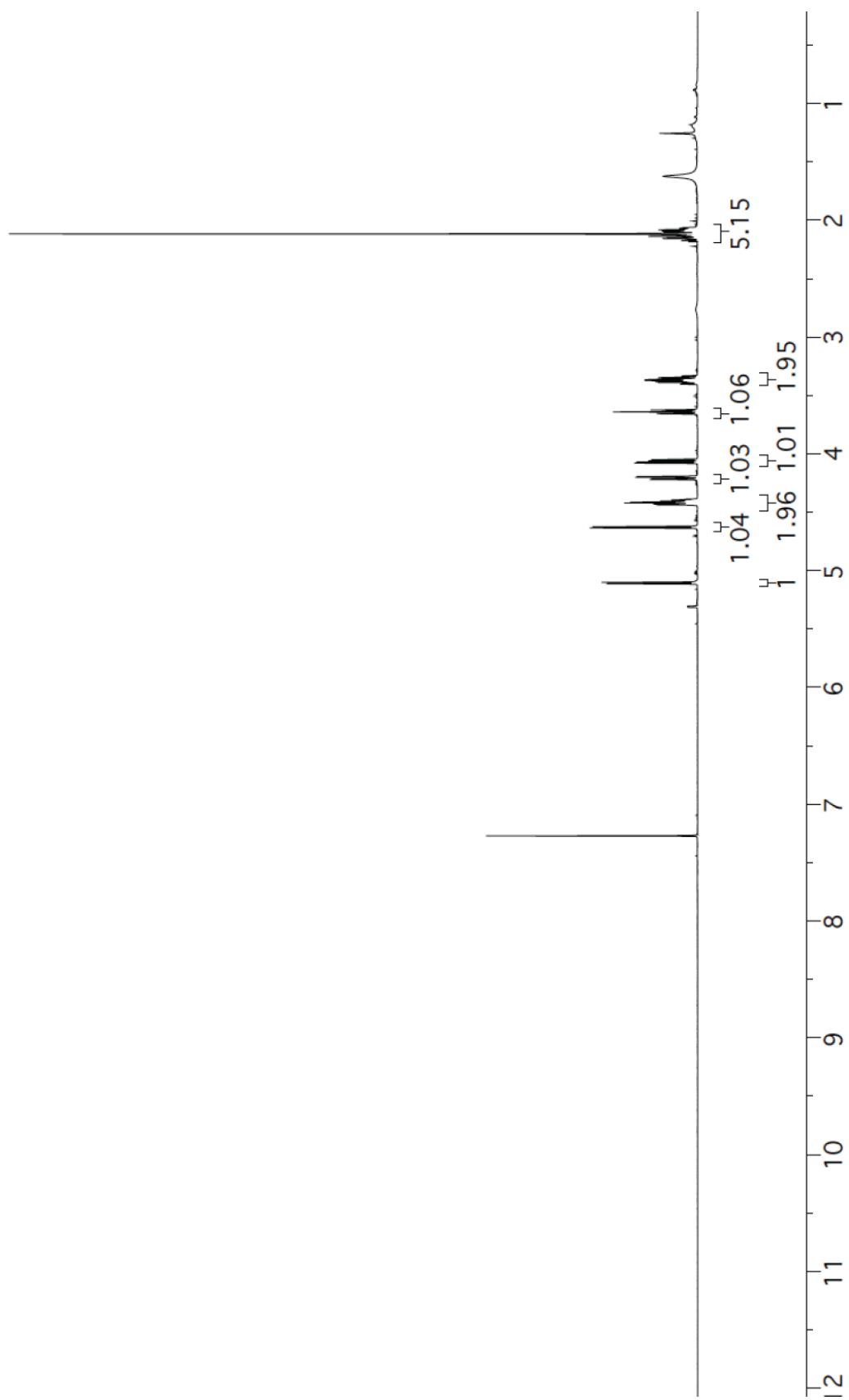
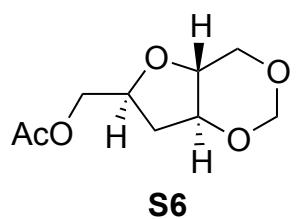


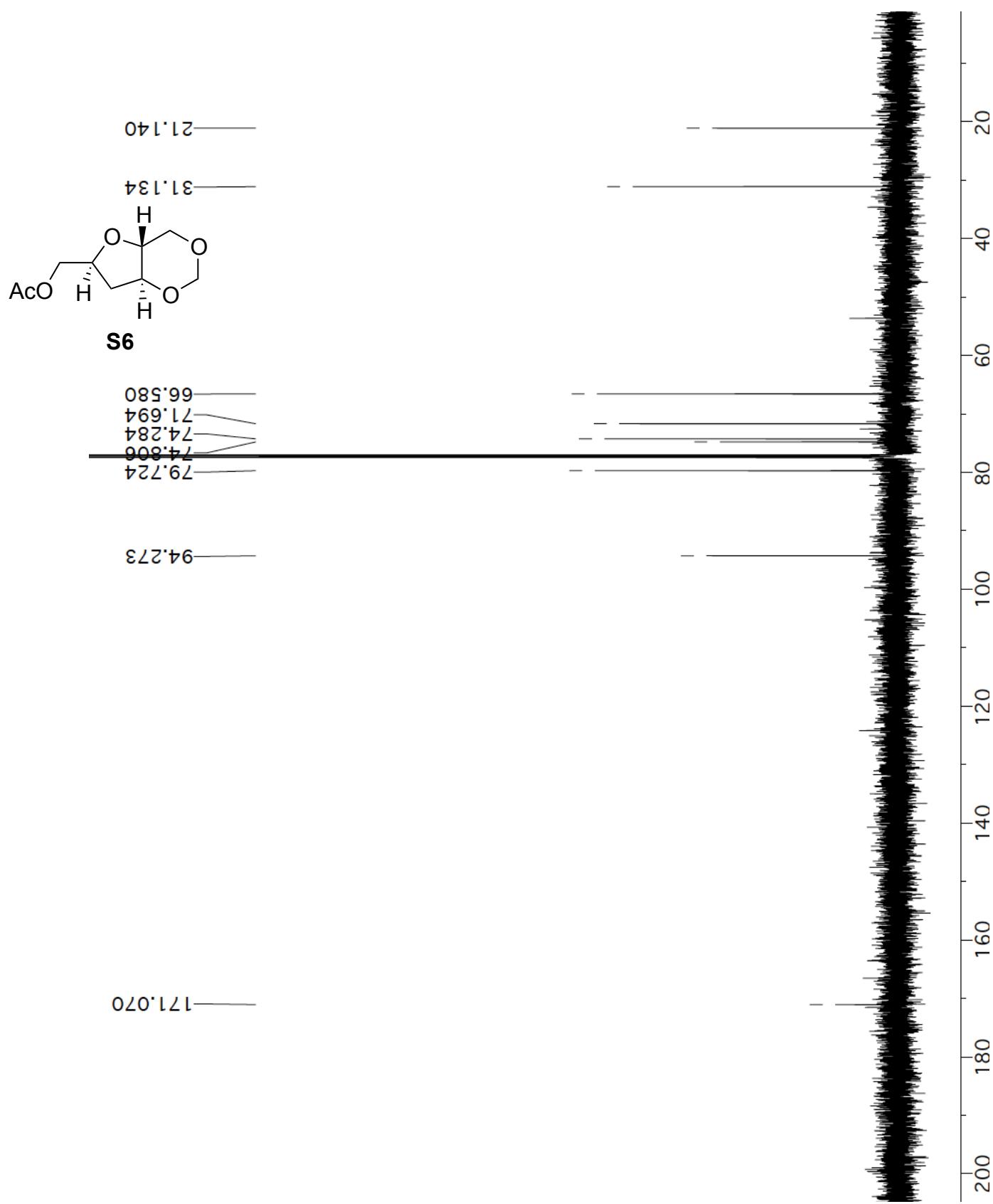




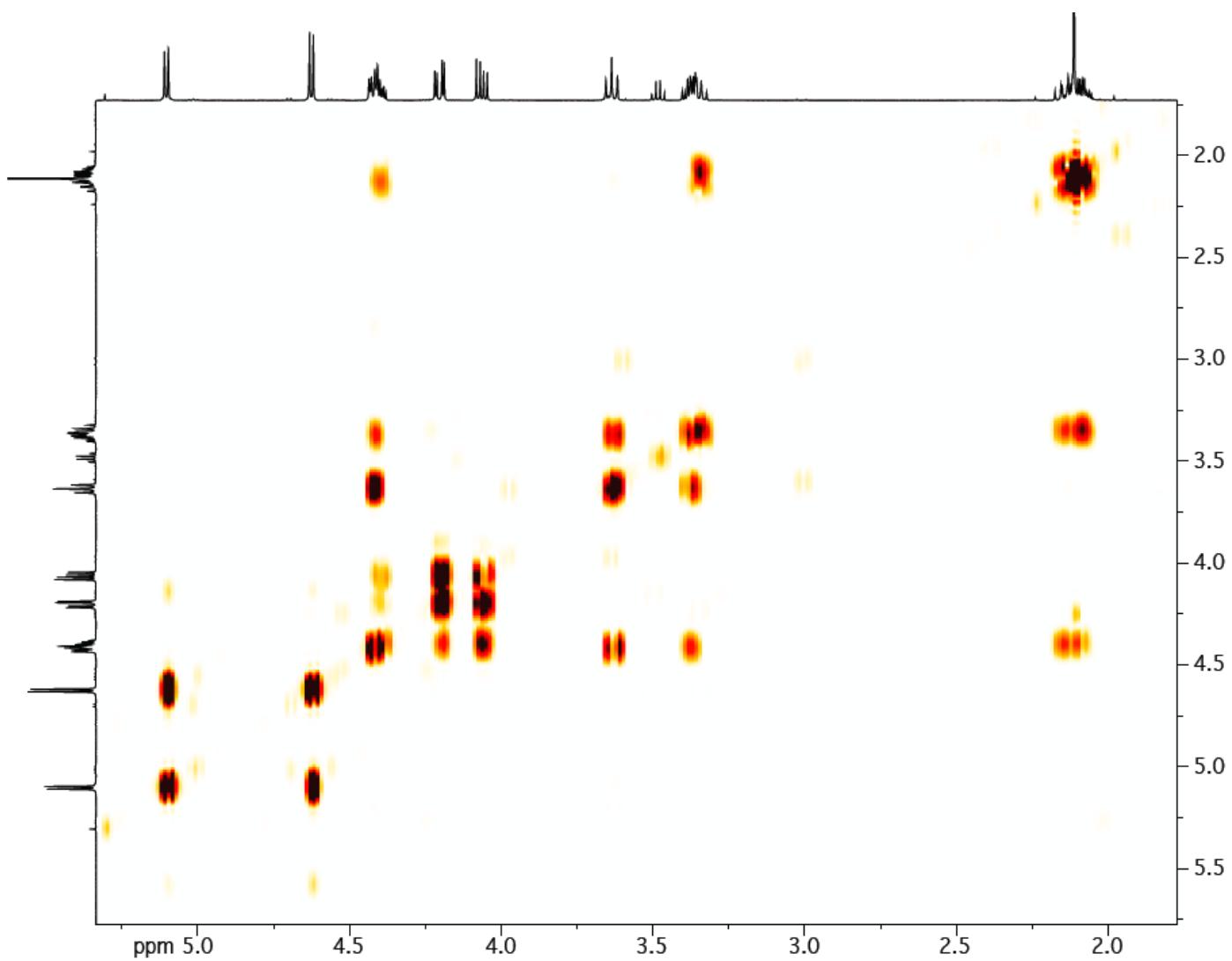
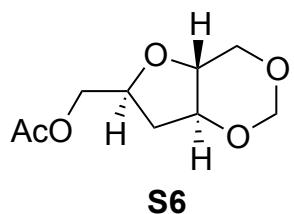
**S5 gCOSY**

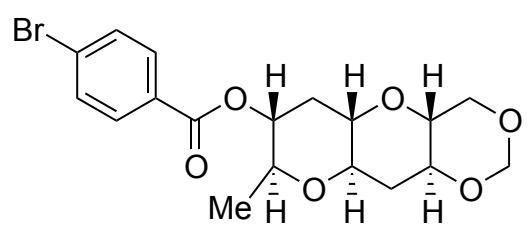




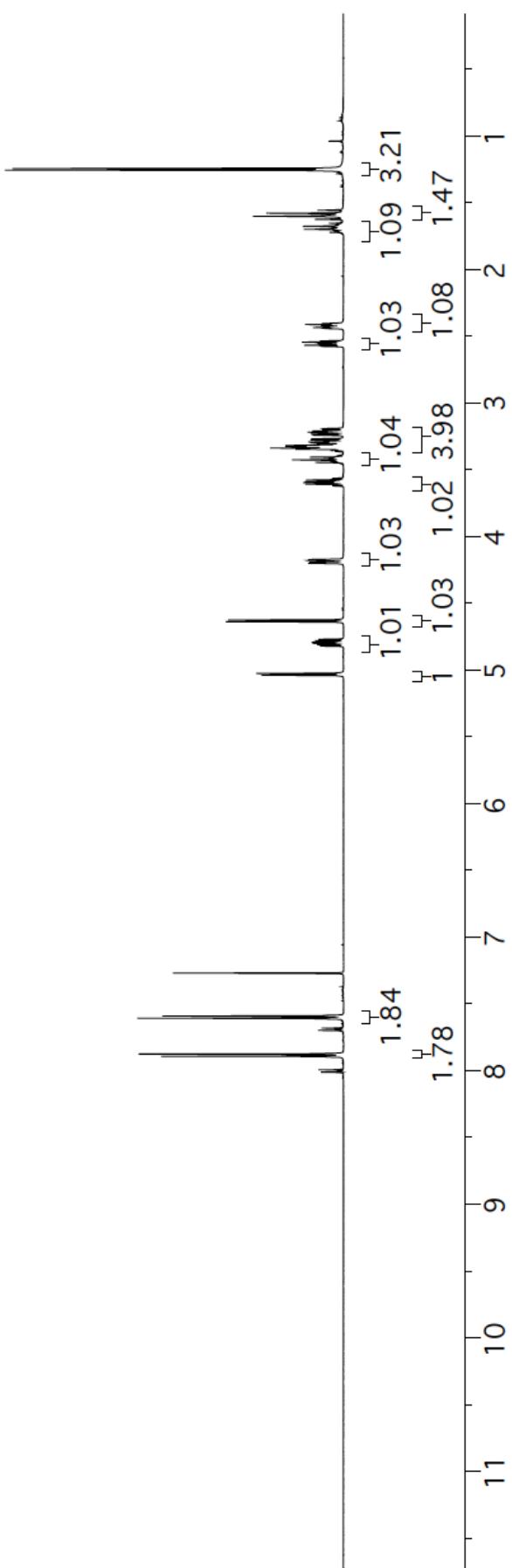


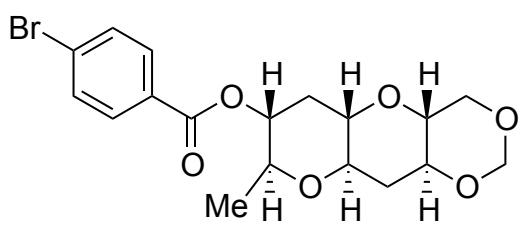
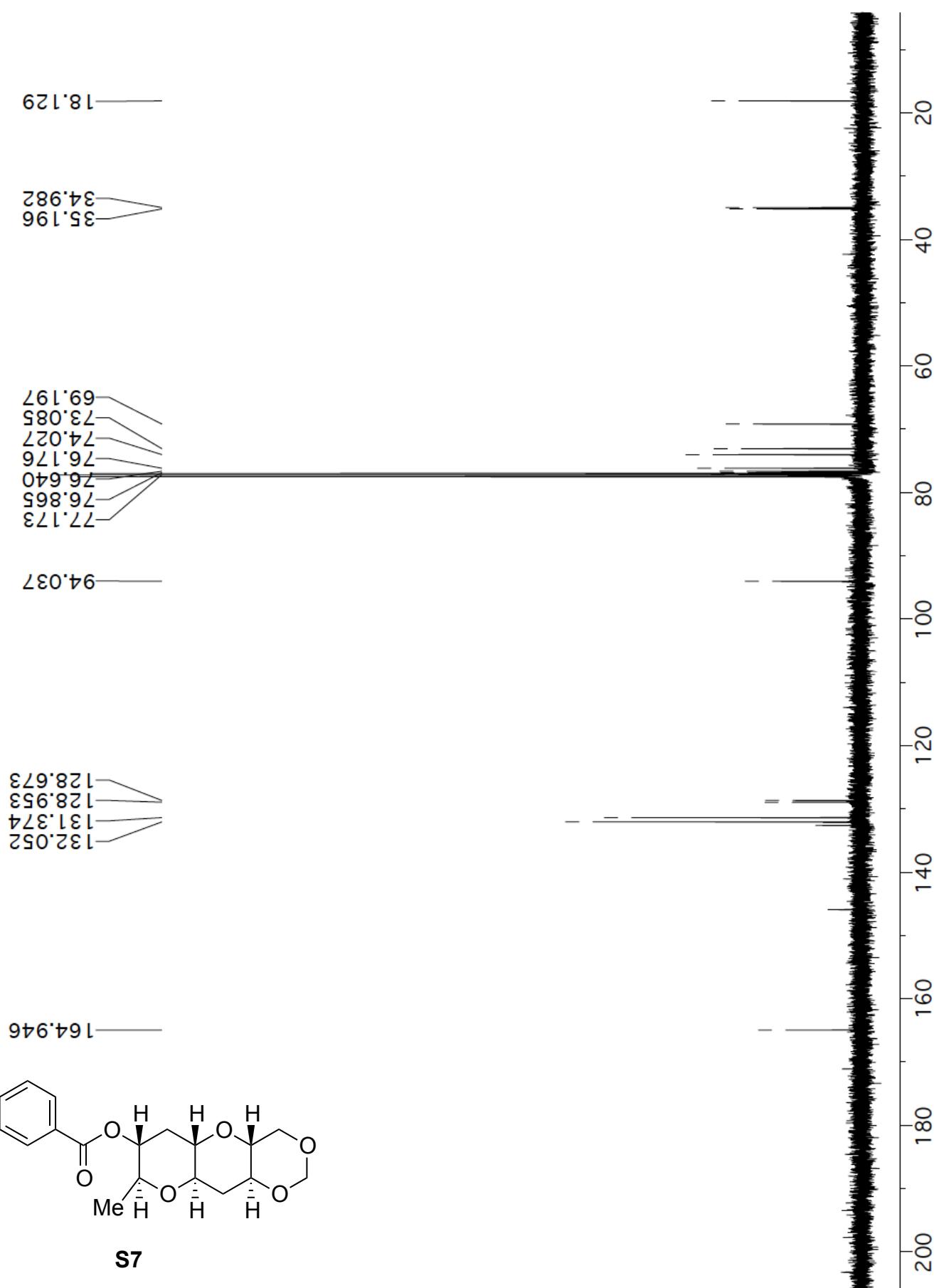
**S6 gCOSY**

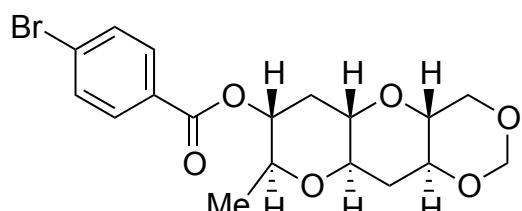
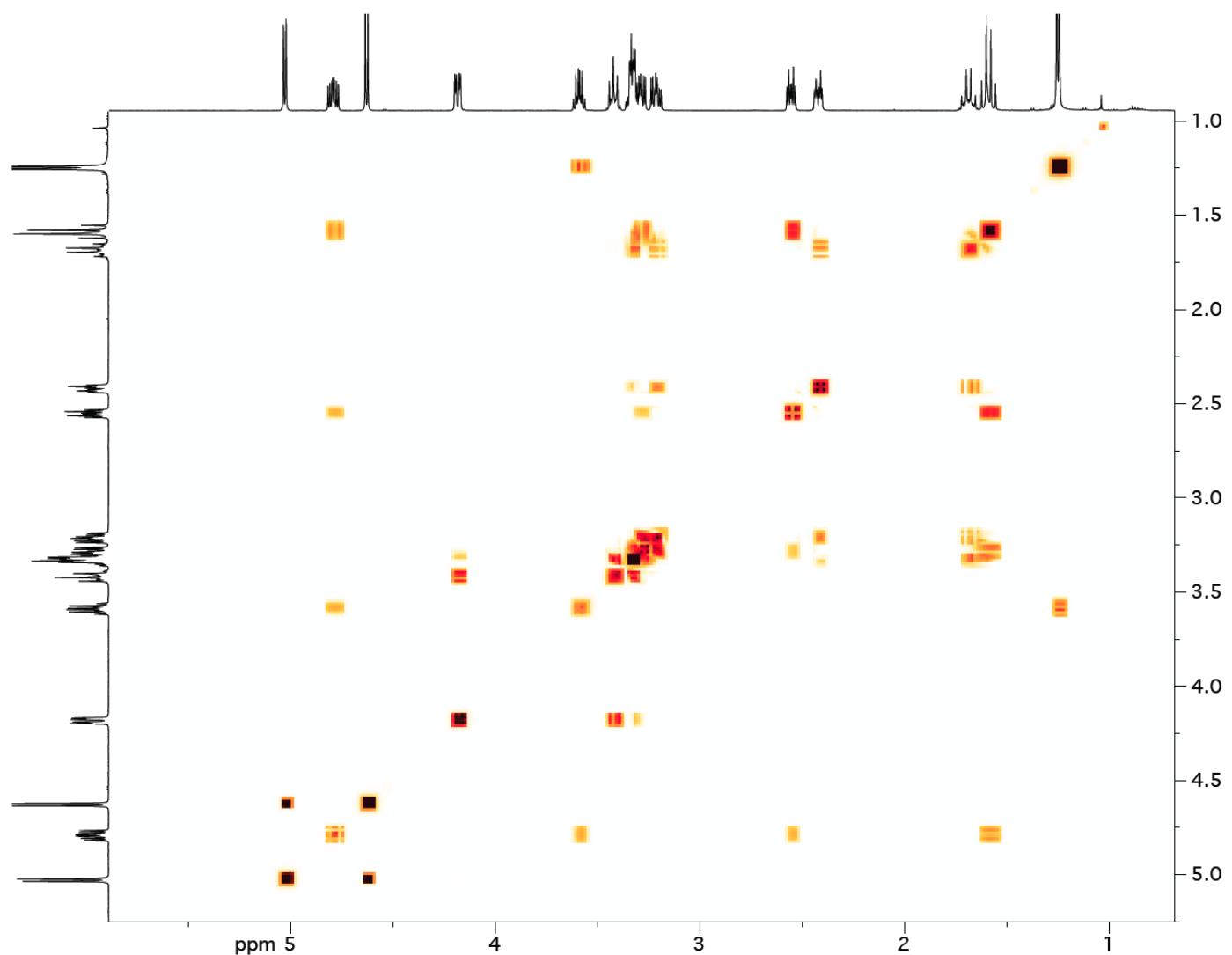




S7





**S7 gCOSY****S7**

## **Selected GC Data**

## GC Conditions

Column: Supelco Chiraldex™ G-TA 30 m x 0.25 mm x 0.12  $\mu\text{m}$  film thickness

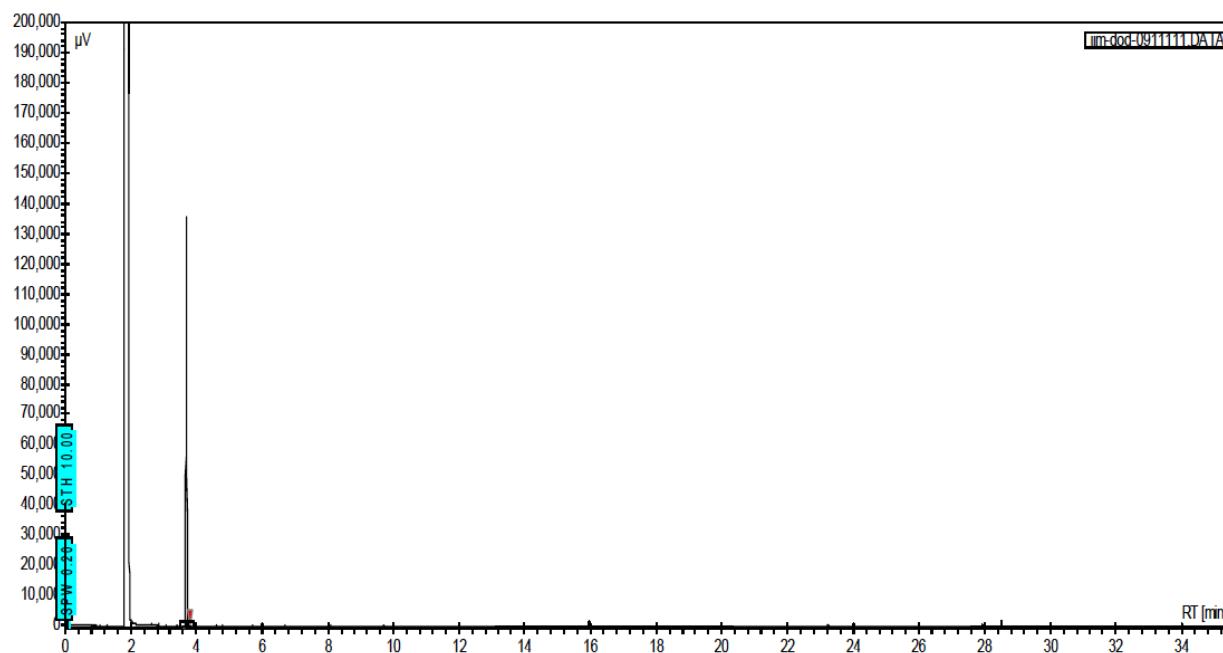
Injector: 50:1 Split ratio, 250 °C

Conditions: 125 °C for 10 min, then 2 °C/min to 150 °C, then 10 °C/min to 180 °C, hold at 180 °C for 10 min. Flow rate of 1 mL/min

Detector: FID, 250 °C

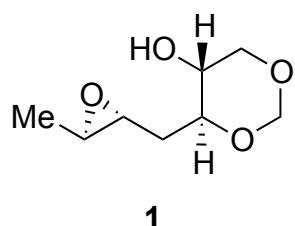
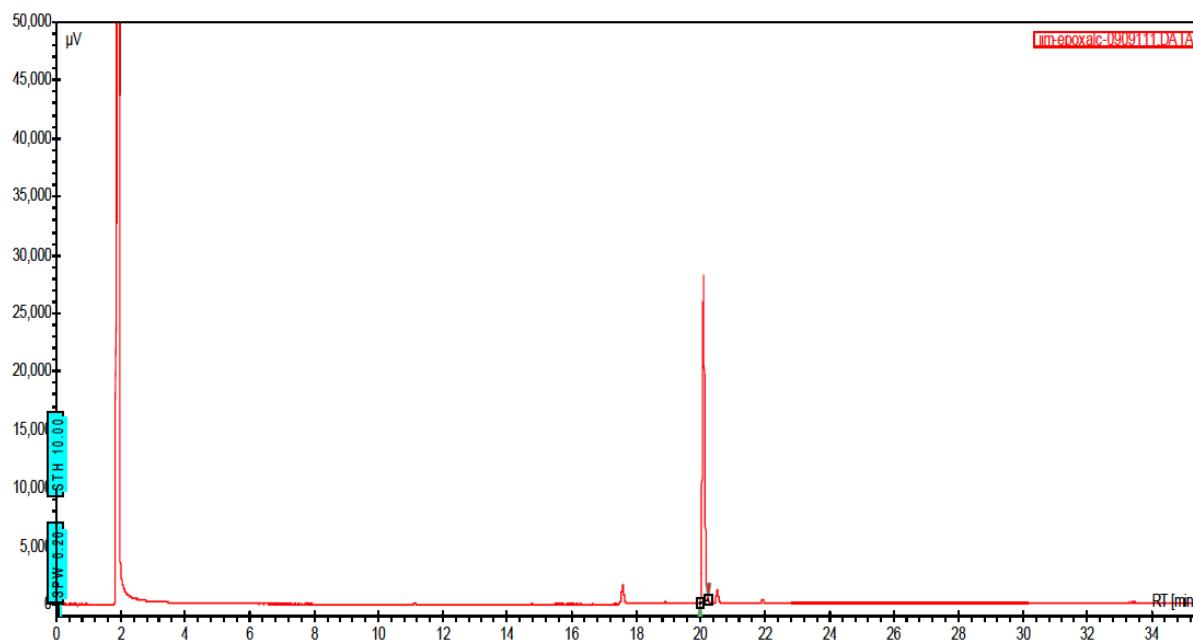
## Retention Times

### Dodecane standard



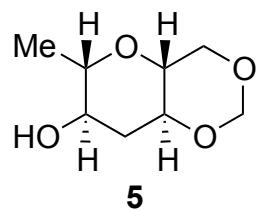
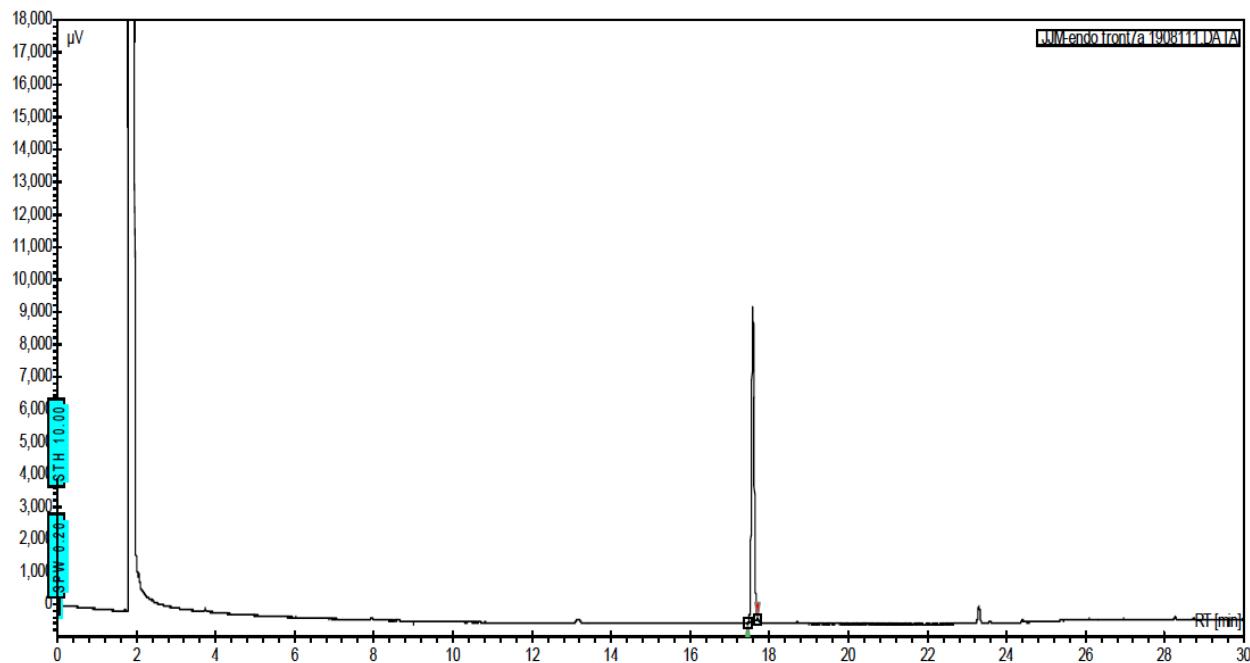
### Peak results :

jim-dod-0911111.DATA [Front (FID)]						
Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	3.70	100.00	135667.5	4397.0	100.000
Total			100.00	135667.5	4397.0	100.000

**1****Peak results :**

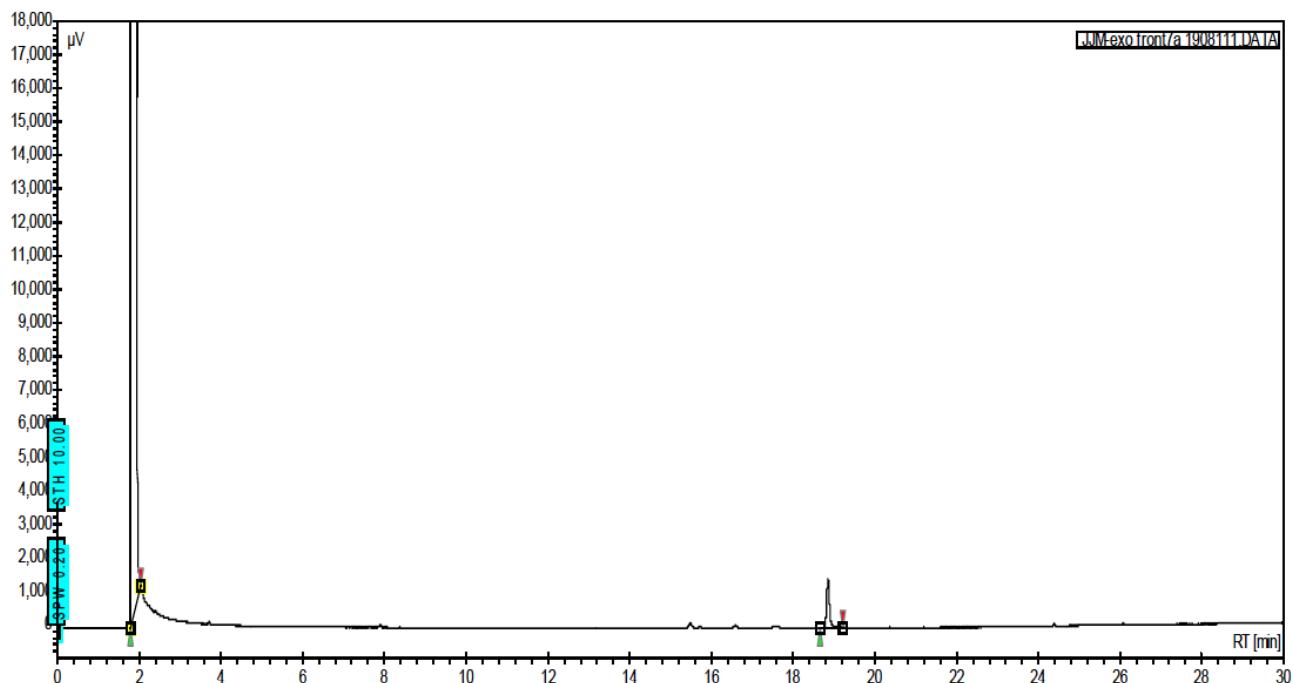
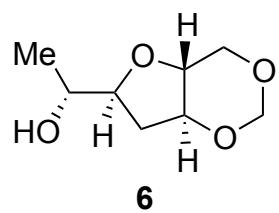
jim-epoxalc-0909111.DATA [Front (FID)]

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	20.09	100.00	27975.1	2361.7	100.000
Total			100.00	27975.1	2361.7	100.000

**5****Peak results :**

JJM-endo front7a 1908111.DATA [Front (FID)]

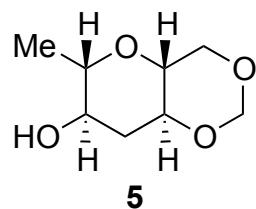
Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	17.59	100.00	9677.5	766.1	100.000
Total			100.00	9677.5	766.1	100.000



### Peak results :

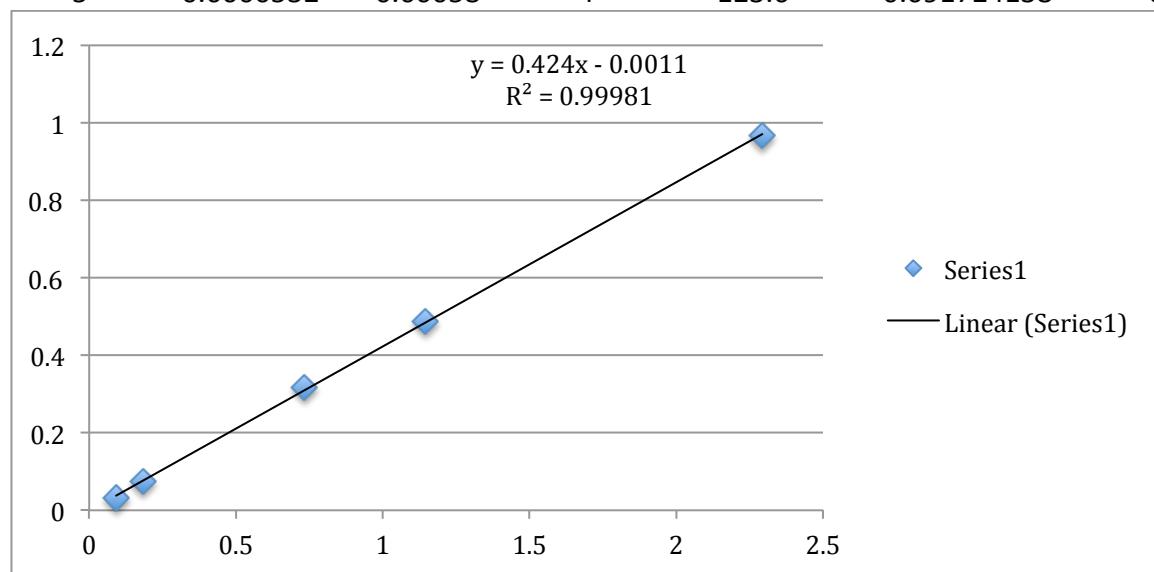
JJM-exo front7a 1908111.DATA [Front (FID)]

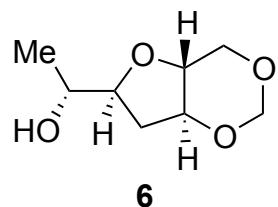
Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV·Min]	Area % [%]
1	UNKNOWN	1.84	99.99	53919132.4	1685113.2	99.993
2	UNKNOWN	18.86	0.01	1464.7	123.7	0.007
Total			100.00	53920597.2	1685236.9	100.000

**Calibration Data**

Curve Endo  
50:1 split ratio  
Starting Material

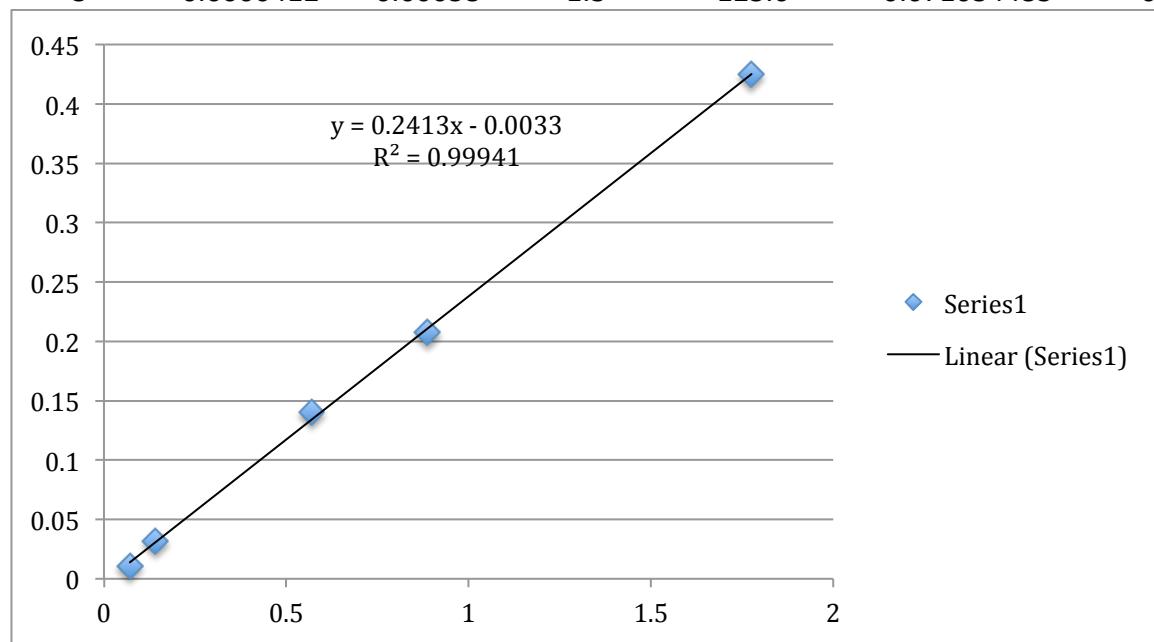
Sample	[SM]	[STD]	Area SM	Area STD	C(SM)/C(STD)	A(SM)/A(STD)
1	0.0001064	0.00058	9.8	130.3	0.183448276	0.075211051
2	0.000426	0.00058	39.8	125.2	0.734482759	0.317891374
3	0.000665	0.00058	59.5	121.9	1.146551724	0.488105004
4	0.00133	0.00058	131.4	135.8	2.293103448	0.967599411
5	0.0000532	0.00058	4	123.6	0.091724138	0.03236246





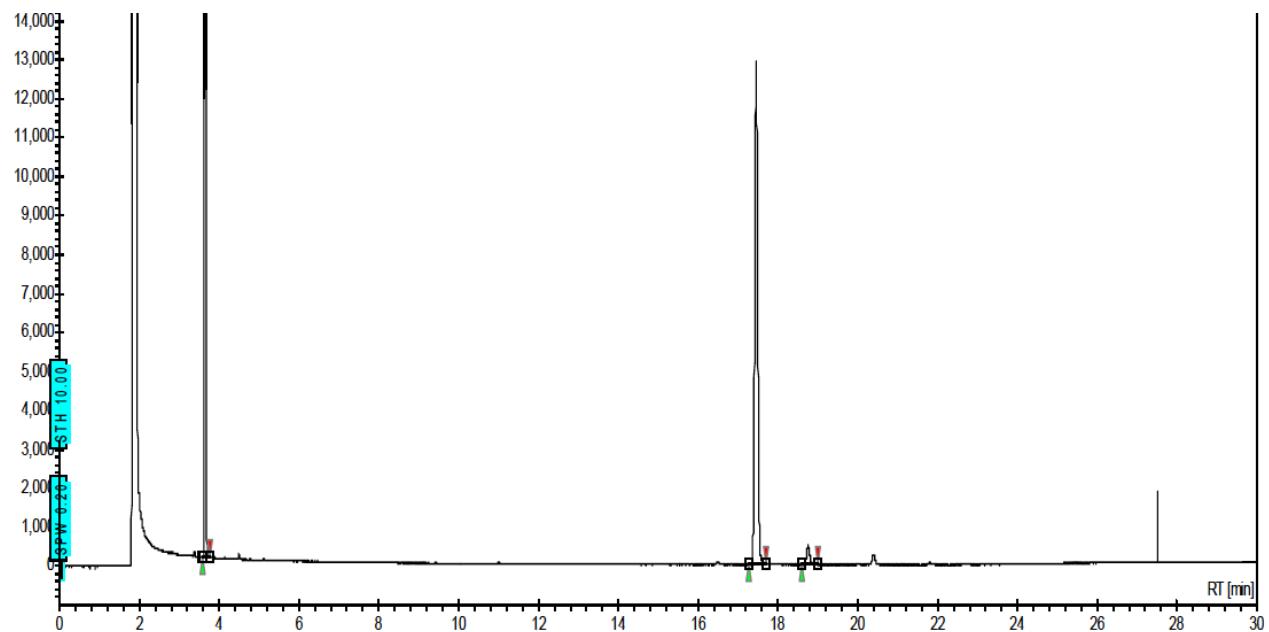
Curve Exo  
 50:1 split ratio  
 Starting Material

Sample	[SM]	[STD]	Area SM	Area STD	C(SM)/C(STD)	A(SM)/A(STD)
1	0.0000824	0.00058	4.1	130.3	0.142068966	0.031465848
2	0.00033	0.00058	17.6	125.2	0.568965517	0.14057508
3	0.000515	0.00058	25.3	121.9	0.887931034	0.20754717
4	0.00103	0.00058	57.7	135.8	1.775862069	0.424889543
5	0.0000412	0.00058	1.3	123.6	0.071034483	0.010517799



## Representative Traces

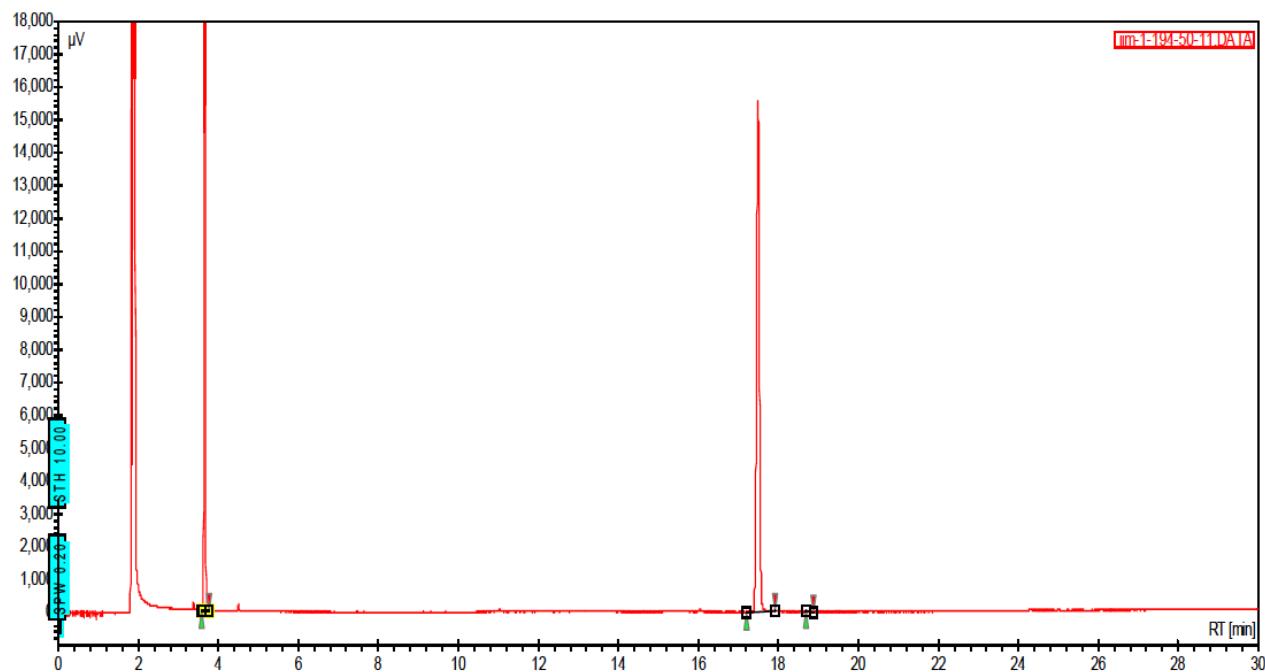
### Cyclization at 70 °C in dH<sub>2</sub>O



### Peak results :

jim-2-8-25to11.DATA [Front (FID)]

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	3.66	67.00	74781.4	2282.4	66.996
2	UNKNOWN	17.46	31.74	12893.2	1081.4	31.744
3	UNKNOWN	18.76	1.26	502.3	42.9	1.260
Total			100.00	88176.9	3406.7	100.000

**Cyclization in presence of  $\text{BF}_3 \cdot \text{OEt}_2$  at  $-78^\circ\text{C}$** **Peak results :**

jjm-1-194-50-11.DATA [Front (FID)]						
Index	Name	Time [Min]	Quantity [% Area]	Height [ $\mu\text{V}$ ]	Area [ $\mu\text{V} \cdot \text{Min}$ ]	Area % [%]
1	UNKNOWN	3.68	70.35	111489.6	2987.5	70.354
2	UNKNOWN	17.50	29.62	15570.3	1257.6	29.617
3	UNKNOWN	18.79	0.03	18.1	1.2	0.029
Total			100.00	127078.0	4246.4	100.000